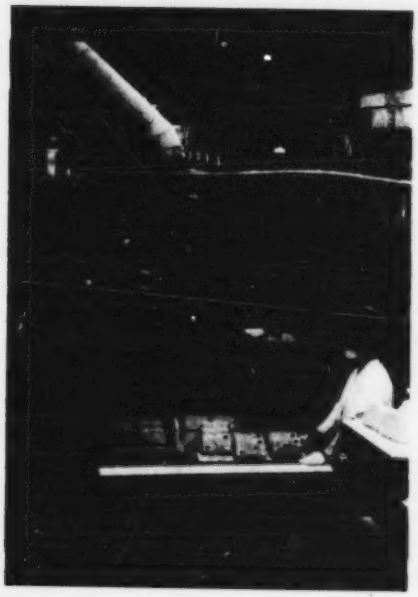
INDUSTRIAL MINERAL
BACKGROUND PAPER 14



MICROWAVES AND MINERALS

I. TECHNOLOGY REVIEW

II. TESTS OF ONTARIO'S INDUSTRIAL MINERALS

Ontario Ministry of Northern Development and Mines

Energy, Mines and Resources Canada

Industrial Mineral
Background Paper #14

Microwaves and Minerals

I. Technology Review
II. Tests of Ontario's Industrial Minerals

By:
Atomic Energy of Canada Limited
Research Company, Chalk River, Ontario
and
Voss Associates Engineering Ltd.,
Victoria, British Columbia

1990

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Photo cover inset: An industrial microwave oven integrated in a continuous automated processing plant in Etobicoke, Ontario. Photo courtesy of the Ontario Ministry of Energy.

NOTE: This background paper does not represent official policy and the views expressed herein are not necessarily the viewpoint of the Governments of Canada and Ontario.

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Executive Summary

THE REPORT REVIEWS THE MICROWAVE HEATING AND DIELECTRIC literature on minerals, rocks, ceramics and related materials. In accordance with the guidelines of this review, ores are only considered with reference to mineral constituents or mineral processing. Microwave heating studies reported in the literature have been confined to 2.45 GHz; no data have been found at 915 MHz. This is also true for the recovery of metals from their ores, with apparently only one important exception which contains data relevant to this study. Extremely high power densities have been used for testing samples; only in a few cases are these realistic in terms of actual mineral processing. Certain oxides and ceramics have received detailed microwave heating study. Dielectric data are so far inadequate to assess any mineral process potential, although there are indications that this is changing due to the industrial interest in ceramic processing and, in particular, the importance of thermal seeds as microwave susceptors and interactive heating elements. Testing methods are discussed and it is suggested that the techniques now available will allow the mineral processing industry to examine a wide range of possible solutions to specific problems.

Both the real and imaginary components of the dielectric constant were measured as a function of temperature for each of eight samples supplied by the Ontario Ministry of Northern Development and Mines. These samples were:

- Serpentine
- Nepheline syenite
- Illite clay
- Kaolin
- Vermiculite
- Magnetite
- Talc
- Talc plus 5% binder (sodium silicate)

Samples containing unbound water showed a dramatic drop in microwave absorption (ε'') when the water was evaporated. On returning these samples to room temperature after heating to 800°C, the lower values of ε'' were maintained. For these materials (illite, kaolin, vermiculite, talc + binder) the minimum value of ε'' was at about 200°C and the value increased with increasing temperature.

Samples containing bound water (serpentine, talc), which were expected to lose this water on heating, showed differing behaviour. The serpentine showed a generally decreasing ε'' with increasing temperature and the final room-temperature value after heating was about the same as the 800°C value. The final product after the heating cycle is expected to be close to the formula $3Mg_2SiO_4 + SiO_2$. Talc, on the other hand, showed a continously increasing value of ε'' with temperature and the final value on returning to room-temperature was about the same as the starting value. The formula, after driving off the bound water, is expected to be $3MgSiO_3 + SiO_2$, i.e. a slightly different magnesium silicate from that produced from the serpentine with fewer magnesium atoms relative to the silica. This difference may account for the differ-

ences in behaviour of ε''; however, both of these products have generally low values of ε'' compared with the first group of minerals.

Nepheline syenite showed low absorbance of microwaves in the "as-received" powder form; however, melting raised the absorbance over 30 times. The melt was amorphous, suggesting that the lack of crystal structure may bring a new microwave absorption mechanism into play.

Magnetite, as expected, was a strong absorber of microwaves, ε'' increasing by an order of magnitude over the temperature range 20- 800°C, to produce a high temperature loss tangent of > 0.1. The magnetic loss tangent, (μ''/μ'), was also high. These two factors explain why magnetite can be heated so rapidly in a microwave oven.

These tests have shown that the technique proposed is an effective and accurate method for obtaining fundamental microwave properties of materials. The information obtained is indispensable for the search of microwave activated mineral processing.

The Canadian contribution to research on both microwave heating effects and dielectric responses of natural solids over the last 25 years is impressive. This report represents a continuation of that effort.

Part One: TECHNOLOGY REVIEW

By:
Voss Associates Engineering Ltd.

1. Review of Industrial Microwave Heating Applications

THE USE OF ELECTROMAGNETIC ENERGY FOR INDUSTRIAL processing represents a small and very specialized aspect of electroheat. A classification of the subject is shown in Figure 1.1 [1]. The industrial heating frequencies in the electromagnetic spectrum are shown in Figure 1.2 [2]. The inset table gives the four most important frequencies: two in the radio frequency (rf) band, two in the microwave band. An economic projection for microwave applications is given in Table 1.1 [2-5]

A 1985 detailed analysis of the applications of rf and microwave has been given by BNCE [2], in terms of rf and microwave feasibility and known commercial applications, with extensive references. The majority of the standard industrial applications are in the food industry. An analysis has been made by Sanio [4]; his tables list the foods processed, together with a description of the method and relative advantages. Economic models with wide applicability are given by Metaxas and Meredith [6] and Sanio [4], the latter including a list of the major equipment suppliers.

Jones [5] has discussed the slow industrial development of both rf and microwave processing over the last 25 years. Between 80 and 90% of the installed power is currently at radio frequencies, although microwave heating has received the most attention in the laboratory and is now apparently growing at a greater rate. This is, in part, due to the availability and impact of domestic microwave ovens, sales of which are now approximately one million per month in the U.S. alone (see Figure 1.3). Whereas microwave applicator design is considered more flexible, rf is still less expensive. Both require extensive development for any particular application, which can only be justified in cases where the market potential is large. The major industrial microwave markets (for which standard equipment is available) are food tempering, pasta drying, rubber curing, textiles, and ceramic processing (see Table 1.1); however, specialized areas such as drug drying, sample analysis and the preparation of rare materials now also command large R & D budgets. There are many other important small-volume applications; these tend to be highly specialized and many users are understandably secretive. Gerling Laboratories publish a list of U.S. patents issued each year in the subject [7] and the International Microwave Power Institute has published a 20-year index of some 2000 articles [8]. Almost every drying, curing and plasma process has been considered. A slow development over the last 25 years is now accelerating.

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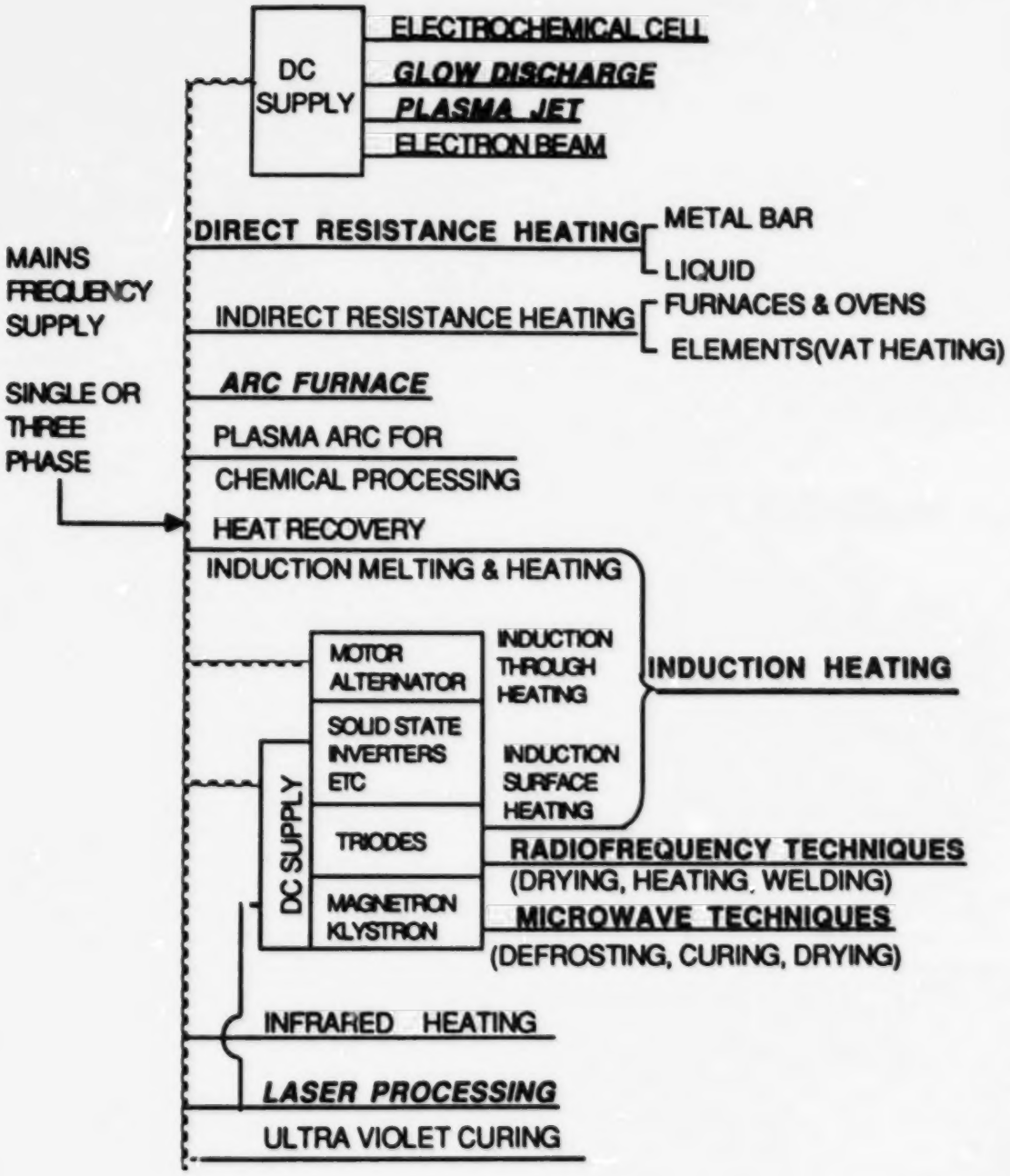


Figure 1.1
Classification of electricity utilization processes. Note: processes shown in bold are part of electromagnetic heating while processes shown in bold italic are part of plasmas.

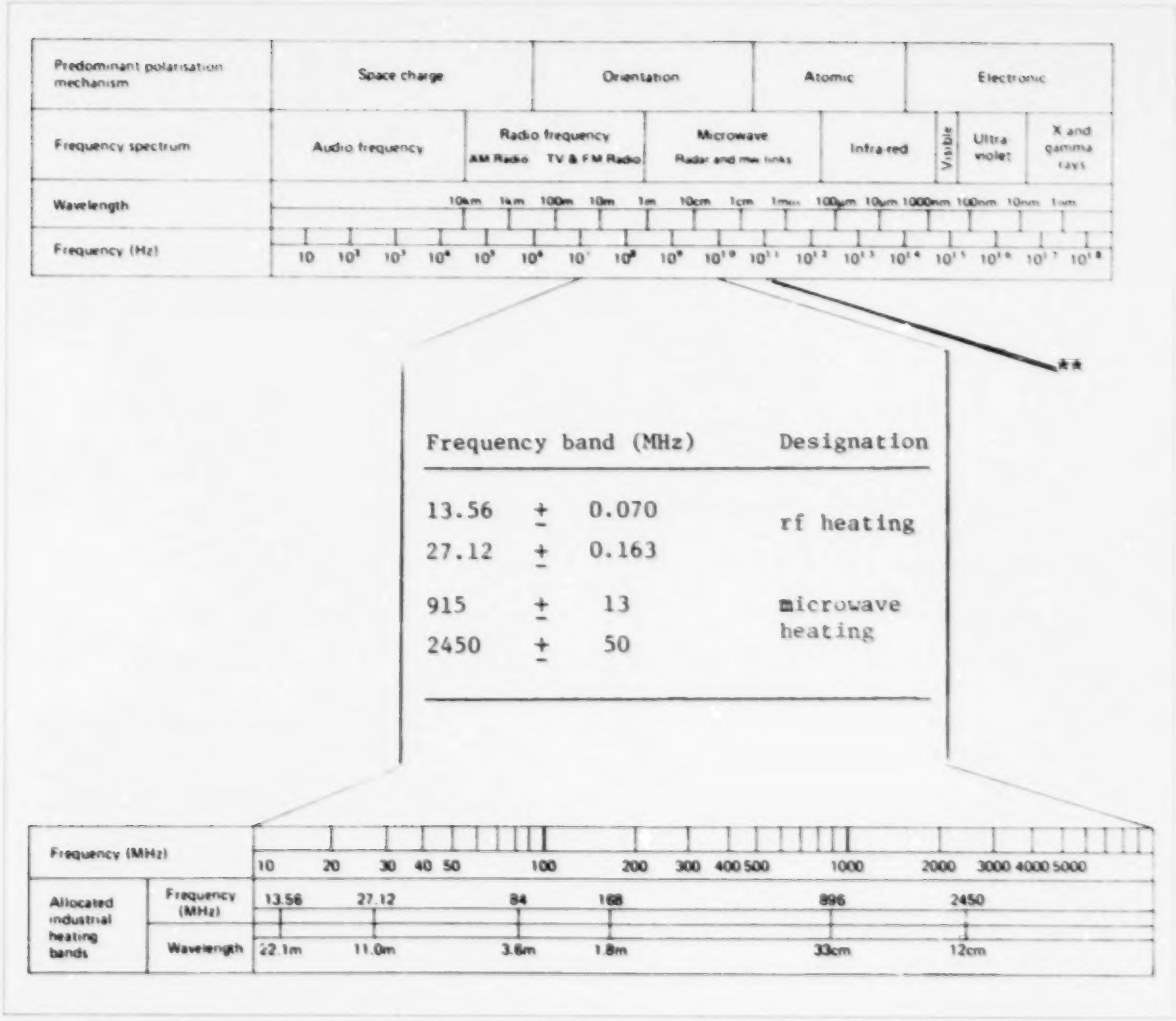


Figure 1.2
Industrial, Scientific and Medical (ISM) allocations in the electro-magnetic spectrum; four most used industrial bands inset. (From 2) **Higher frequencies are also used in ceramic processing (3). Not all applications are confined to ISM bands; in these cases, leakage (noise interference) prevention is a major design requirement.

Table 1.1
Industrial microwave applications

in the major areas where equipment has become semi-standardized; world-wide; based on (3,4); numbers rounded off.

Area	Microwave power installed/yr MW	5 year market potential 1989-1994; $M
Food: tempering, industrial[a,d] cooking, pasteurization, drying, baking	3-5	60-70
Ceramics[b]	2	50
Elastomers: drying tempering,curing	2	55
Wastes: pollution, reclamation,nuclear glassification	3.5	50 (?)
Forest Products:[d] glueing,laminations, drying	0.5*	15
Composites: forming,curing	0.5*	9
Textiles: drying,curing[c]		7
Medical: biological, hyperthermia-cancer therapy[e]	0.03*	5

[a] See [4] for detail. [b] See [3] for detail. [c] See, for example, [2]. [d] For rf microwave comparative volumes see [5]. [e] Many small systems in clinical use. Asterisk [*] indicates our estimate.

The components of an industrial microwave processing system are:

- Power supply: ac to dc high voltage (3-14kV)
- Generator: magnetron or klystron
- Circulator + waveguide : couples power to applicator; circulator absorbs any reflected power. Typical waveguide sizes (rectangular): at 915 MHz 24.7 x 12.38 cm; at 2,450 MHz 10.92 x 5.46 cm, 8.64 x 4.32 cm and 7.21 x 3.40 cm.
- Power monitor and control system: Generally built into the power supply
- Applicator:
  a) Resonant cavity:single mode:circular or rectangular (e.g. plasma, filament curing etc.); multimode
  b) Quasi-resonant large tunnel
  c) Travelling-wave: material inside a waveguide
  d) Fringe-field: material on the surface
  e) Horn: expanded waveguide,usually fed into (b)
- Wavetraps and safety monitors: Several magnetron generators can be coupled to one applicator. Various types are illustrated and discussed in [6], which is a key reference text.
- Auxiliary equipment: Many hybrid systems are used and there is considerable design flexibility for including air jets, infrared, and, for example, magnetic separation equipment.

Generators at 915 mHz, in general, use magnetrons, with power outputs from 25 to 60 kW and approximately 250 kW in one tunnel possible. Open applicator arrays (slotted waveguides and horns) have been proposed, for example, for asphalt curing [9]. Thin materials, for example, nylon drying, use either travelling-wave or resonant structures; temperature control is achieved in the latter case by feedback from the cavity to the generator; and chemical-plasma reactions result from very high field strengths achieved in small resonant applicators. Some of the most successful applications use only a small percentage of microwave energy in processing a material.

With electromagnetic heating, design flexibility is achieved at the higher (microwave) frequencies, in part due to the lower field strengths required for any given power density. Irregular shapes and changing load sizes, in general, require the use of microwave frequencies. Capital and operating costs increase with frequency: both are typically double at 915 and 2450 MHz in comparison with 27.12 MHz; however, microwave heating is often a more efficient energy conversion process, but there are exceptions, one being the drying of sheet materials of fixed geometry [5].

Sanio has given an economic analysis of microwave processing which applies to many applications [4]. Capital costs range from $2000/kW to $5500/kW (Canadian) depending upon the complexity of the integrated system. A typical 100 kW, 915 MHz system now costs about $350k for meat or butter tempering. Power tube (magnetron) life ranges from 2000 to 7000 hours. The replacement cost of a magnetron and circulator effectively more than doubles the cost of electricity. Each application, therefore, requires a careful analysis; it is doubtful if any system once standardized can be installed for less than $2/W (nameplate) and operated for less than twice the cost of electricity per watt-microwave coupled to a load. A great many development programmes, particularly in drying applications, did not consider this early enough and an expensive solution has looked at some problems unsuccessfully over the last 25 years.

Penetration depth (resulting in rapid, deep heating) and selective heating are important microwave advantages [6]. Others are:

- increased production rate
- automation
- space saving
- raw material cost reduction
- energy saving
- reduction in the cost of other materials (e.g. water)
- process control (quality, material flexibility, temperature, emissions)
- new materials and processes (e.g., in ceramics).

The major offsetting factor for rf and microwave are the cost of research and development, skilled labour, operating and maintenance. The latter is particularly true in the primary industries.

Many potential advantages arise in the ceramics industry, some of which may apply to mineral processing studies. Rapid and controlled heating in substances with low to very low ther-

mal conductivities are the major reason. Interactive and differential heating between materials and the use of "thermal seeds" within materials are today major areas of microwave heating research and development. This activity has arisen in the last ten years; it relates to ceramic drying [see, for example 10], new ceramic materials [3], new chemical processes [for example 11] and nuclear fuel pellets [11, 12]. However, the earliest reference to thermal seeding for large-scale microwave processing was in 1962, in ore treatment [13].

During the study we have not found any data from even prototype microwave systems in the mineral industry. Although many microwave ore processing patents have been issued which provide useful data on oxide and carbide heating rates (and the effects of other additives—thermal seeds), the first significant microwave processing patent which would apply directly to minerals was issued in 1987 [14a], according to our Dialog and Derwent system searches. It is logical for the mineral industry to consider valuable materials first, in this case kimberlite; in [14a] a new microwave technique is described whereby materials are selected according to their relative temperature rise.

Extensive laboratory heating tests have been performed on mineral samples and chemicals at 2.45 GHz but we can find only one at 915 MHz [14b]. Although that study again relates to ores, the relative heating rates involve minerals and common impurities. The conclusion to be drawn from [14a,b] is that 2,450 MHz is more selective than 915 MHz - and that even higher microwave frequencies would be desirable. This may be more generally true than is immediately apparent. A careful analysis of mineral dielectric data from geophysical exploration sources (available only at ambient temperatures) is required, together with extensive measurement at higher temperatures, before any frequency comparisons can be made. 915 MHz is, in terms of physical and power penetration factors, a more desirable frequency; it is also a little less expensive and slightly more energy efficient for large systems than is 2,450 MHz.

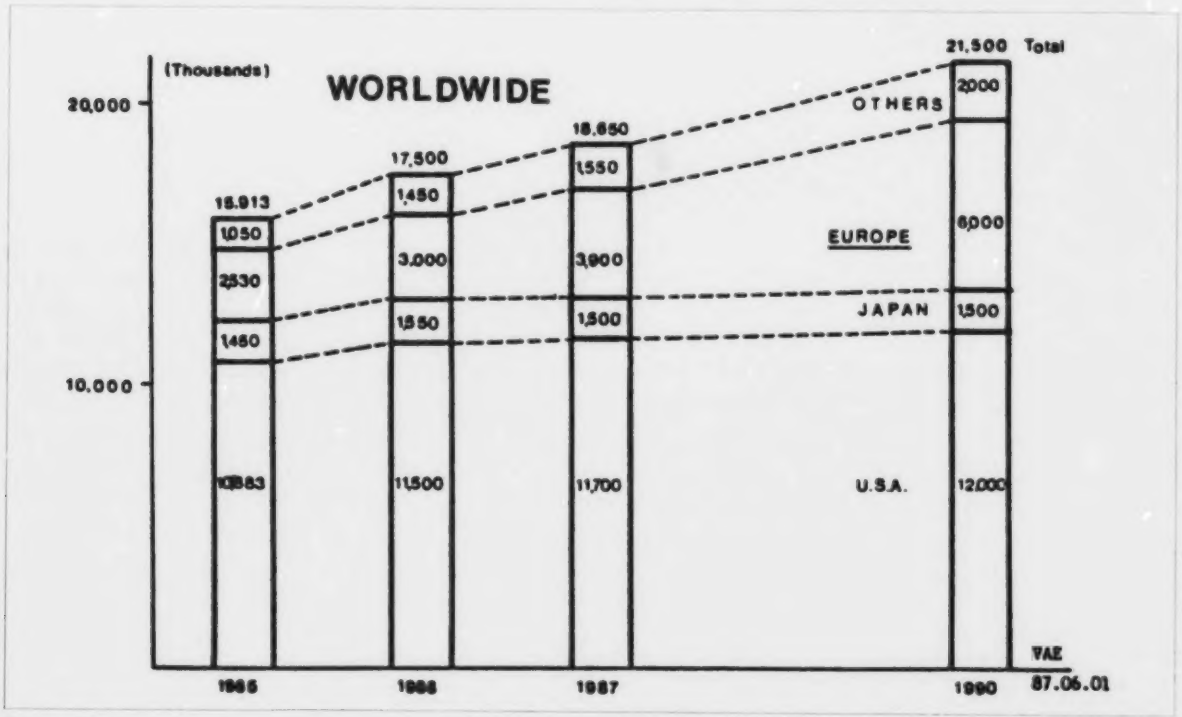


Figure 1.3
Worldwide annual sales of domestic microwave ovens; 1985, 1986 (shipment compilations - best estimate), 1987 (predicted early in 1987) and projected 1990. Figures shown are in thousands, to a total of 21.5 M projected in 1990. (From *Electromagnetic Energy Reviews*, 1988.v.1,no.2,p.24.)

2. Applications Related to Minerals and Electro-magnetically Similar Materials

Minerals and Ores

"This invention relates to methods and apparatus for treatment of ores and more particularly to methods and apparatus using high frequency electromagnetic fields to cause chemical decomposition of one or more compounds in the ore ...

It should be noted that the system of [Figure 2.1] and also the other systems disclosed herein may be used in the conversion of hematite ore or magnetite and may be used, for example, in conjunction with siderite, goethite, limonite and many other types of ore....

To increase the moisture content of the ore granules, to thereby increase the conductivity thereof and internal heating by the microwave field, water may be supplied .... It is also desirable with many ores to add fuel there to ... a gaseous fuel or reductant, such as carbon monoxide, may be supplied."

From U.S. Patent 3,261,959, L.H. Connell et al. Filed 1962, issued July 1966. [13]

The patent process cited above refers to the intense heating action of microwaves on magnetite and, to a lesser extent, hematite. Together with some other oxides, either as common impurities or mineral bodies, and metal films, they dominate the current industrial interest in susceptor or interactive heating materials. Recent proposals by the U.S. Bureau of Mines include this use of magnetite as an activator for heating other inert minerals [15-17], the heating responses of which are discussed in this report from several sources. The most valuable source—and closest in technique to the samples analyzed experimentally in Part Two of this study—is due to Chen *et al* [18] in 1984.

In the intervening years a number of U.S. and foreign patents were issued, describing the use of microwave heating in the processing of specific ores, and the drying of non-ore concentrates. Many of these patents provide information on other possible mineral processing systems and give some data on the properties of metal oxides, all of which are useful to this study: the latter because some metal oxides and other compounds occur in minerals, either as impurities or major constituents. The link is valuable, in particular, where the iron oxides are concerned. Although the absorption mechanism in rocks and minerals is primarily due to metal oxides and sulphides, structure, bound water and other impurities appear to play an important role as well.

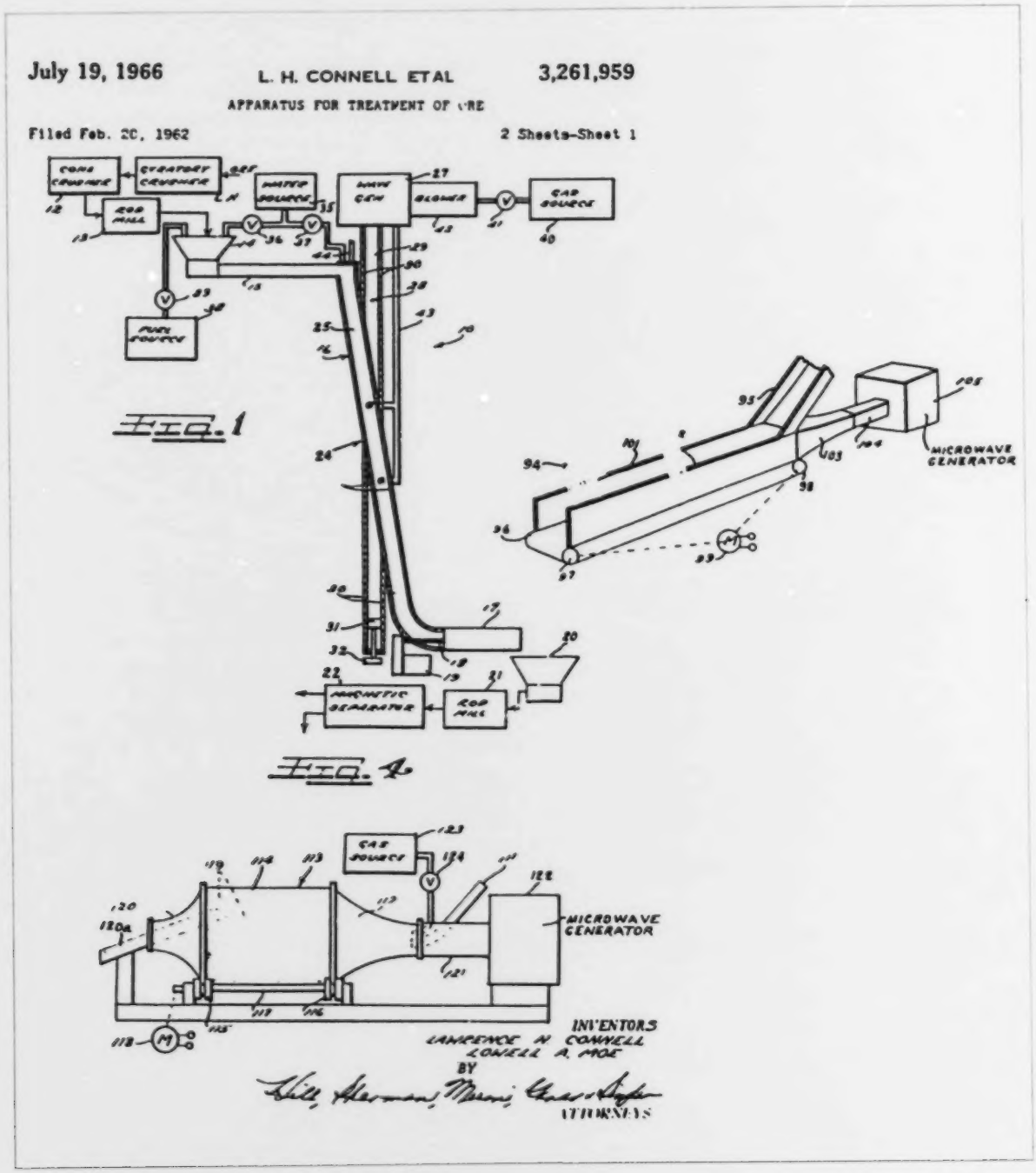


Figure 2.1
An early microwave ore treatment patent with wide applicability to mineral processing.

Trace impurities in minerals (which are obviously variable—see ahead and the geological analyses of Ulaby [19]) can have a major effect on microwave as well as optical absorption. Put simply *and by way only of example*, de Beers' microwave heat-scan system for kimberlite [14a] would probably destroy the rare type 2b diamonds. Kimberlite would heat more rapidly than gabbro; diamonds and garnet, etc. would not be affected—*except for* the only naturally occuring (and very

rare) room-temperature, semi-conductor diamond (type 2b, blue) which is carbon "doped" with boron, a parts per million impurity. This is probably the extreme example in nature of a trace impurity totally altering electrical conductivity, an effect which we *assume* would apply from dc through the microwave spectrum. It is also an interesting theoretical example of interactive heating and thermal runaway. Diamond changes to graphite slowly above ca. 1000°C; graphite is a prime absorber of microwave energy but its absorption characteristics also depend on the manner in which it was formed.

Many mineral applications may follow from these principles, due to microwave data from ore processing, sample analysis, rock cracking through to synthetic minerals (ceramics). Table 2.1 at the end of this section attempts to summarize the relevant developments *in historical perspective* for rocks, ores, minerals and similar materials to the present time. The objective of Table 2.1 is to list the key ideas and references which are relevant to minerals but which arise, in many cases, from related areas.

In attempting to analyze microwave heating and relative heating rates from the literature for minerals and ceramics, three major difficulties arise:

(1) No two laboratory protocols are the same—and several use domestic microwave ovens, *which are not scientific tools;*

(2) Pure materials are only indicative of what can be expected in practice; *in only one report* are chemical analyses given before and after microwave treatment of true mineral samples [18];

(3) The dielectric data base at high temperatures, even for pure solids, is totally inadequate. A possible exception is the metal oxide family. Not even the behaviour of bound water at very high temperatures is understood in, for example, quartz.

An additional (and perhaps not surprising) difficulty is the lack of published data on even prototype or full size microwave preprocessing or sorting systems—if they exist. This is the challenge to the present study—one that is greatly assisted by the 1988 statistical microwave rock study (for prospecting and related areas) by Ulaby *et al* [19]. Although mineral sample analysis by microwave heating—a rapid, controlled and accurate method—is not strictly within the scope of this study, it is included *briefly* in the following as it may aid process analysis for the possible development of microwave systems. It is visualized that any process development would be specialized initially and follow the mineral material and problem-specific approach suggested by the de Beers' patent [14a], requiring an extensive dielectric-thermal properties investigation, an extension of, for example, Ulaby's work for each material *over a wide temperature range*. It is not unfair to say that all microwave heating studies reported to date on mineral and mineral-related materials represent a possible yet undefined solution looking for problems, with one possible exception—a method for removing pyrite from kaolin, which appeared only in one short conference report [20].

Pyrite (FeS_2) particles, as an impurity in kaolin (mainly $Al_2O_3.2SiO_2.2H_2O$), cause black marks on pottery. In seeking a preprocessing method of pyrite removal, Bodem [20] found that, individually, isolated particles of pyrite and kaolin heated "moderately" without chemical change at 2,450 MHz. In nitrogen or an airstream, a homogeneous mixture experienced sparking between FeS_2 particles with the FeS_2 (a semi-conducting material) turning ferromagnetic. With natural kaolin Bodem observed that the FeS_2 acted as centres (seeds) in the heating process, which eventually turned all the material red hot, lumping it into a glassy mass. He observed that the kaolin itself became an active absorber of the microwave energy once elevated in temperature. In order to heat the FeS_2 without fusing the kaolin, he fluidized the bed during microwave heating. The FeS_2 particles were ferromagnetized rapidly at the surface and separated by a magnetic field. The temperature of the kaolin mixture as a whole did not exceed 300°C during the heating process [20]. When impurities are semiconductors at low temperatures, or are triggered to this state by a prior interactive heating mechanism, and a reaction is microwave (or rf) selective, other preprocessing techniques may be possible for minerals. The complexity of the overall electromagnetic heating problem is illustrated in two ways by Bodem's solution. First, for a semi-conducting material such as FeS_2, the microwave selectivity in kaolin may be greater at 915 MHz because Al_2O_3 will have a high-temperature loss factor which is less than its 2,450 MHz value. Secondly, Al_2O_3, (and similar materials) have a thermal conductivity which *decreases* with temperature, thereby increasing the tendency for kaolin to fuse [21]. Finally, it has to be stated, this process would probably not have been discovered from measurements on random samples in either a domestic microwave oven or a very high power density resonant applicator, even though electromagnetic techniques for magnetic enhancement (in ores) were known at the time [22].

Rock Heating, Fracturing and Tunneling

A 1974 study on thermal rock weakening techniques by Laurello *et al* [23] found microwave heating a poor technical solution to the problem—and uneconomic. They did not consider special environments (e.g. tunneling in inner cities) but they made two major contributions to the subject of electroheat in massives. First, they solved the theoretical energy transfer problem for microwave heating simple geometrical formations and applied this to granite formations (their material of fracture interest). Secondly, they did a (1974) comparative economic analysis of rock excavation by lasers, electron beams, microwaves, radiant heaters and torches. It would be possible, from their study, to include the economics of recent microwave plasma torches. In summary, they stated:

> "Analytical predictions of the rock weakening by thermal sources are used to compare the relative costs of enhancing rock excavation by lasers, electron beams,

microwaves, radiant heaters and torches. These estimates indicate that the expense of microwaves is prohibitive while radiant heaters are the least expensive at $0.14/ft^3. Jet torches are also desirable at an energy cost of $0.18/ft^3. Design limitations for the various methods are noted and equipment costs range from $50,000 for electron beams to $300 for flame torches. When energy costs, equipment costs and design limitations are all considered, the jet torch seems the most promising using commercially available equipment. Considerable design effort when applied to radiant heaters could produce an even more efficient system for weakening rock." [23]

It has been stated that patents have been applied for on a microwave plasma torch [83] for mineral extraction applications. Arata et al [24] have described a simple microwave cutting tool with a very narrow, high-temperature plasma beam. Plasma furnaces for refractory materials are well-known [see, for example, 25] and there may well be microwave advantages for solving some of the nozzle size and temperature problems discussed by these writers [24,25].

In 1976 Hoekstra reviewed rock, frozen soil and ice breakage by high frequency electromagnetic radiation [26]. The U.S. Corps of Engineers study is valuable for two reasons. First, it provides a detailed comparative analysis of the penetration of rf and microwave into several formations (sandstone, hard and soft rock, ice). Secondly, it reviews all the Russian work. Hoekstra's summary is given below:

> "Review of the U.S.S.R. literature on rock breakage by high-frequency electromagnetic radiation showed that one area of possibly significant application is excavating tunnels and shafts in rocks of high strength. For rocks of low strengths and in frozen ground, the U.S.S.R. research did not yield promising results. The mechanism that makes use of high-frequency radiation attractive in hard rocks is fracturing caused by thermal expansion some distance behind the air/rock interface. This mechanism, therefore, requires 1) penetration of significant amounts of radiation some distance into the rocks, and 2) concentration of energy absorption at grain boundaries and hairline fractures.
>
> Computations of the effects of radiation as a function or rock type showed that most energy is absorbed at the surface in soft rocks, resulting in very rapid heating of the surface layers, but only small temperature effects beyond the first few centimeters. Computer modelling showed that radiation can penetrate hard rock to depths of 0.5 m, causing gradual temperature rise. The effects of inhomogeneities where energy absorption can be concentrated were not modelled.
>
> In frozen ground, radiation results in the melting of surface layers, and as the Russian results indicate, mechanical tools must remove the thawed surface layers before underlying layers can be exposed.
>
> In general, all investigations lack information on significant parameters, energy absorption as a function of depth, water content, structure, etc. For hard rocks, where both Russian results and computations show that significant applications may occur, it is necessary to conduct a controlled series of laboratory experiments to establish the range of application of the use of high-frequency energy in rock breakage." [26]

Soil stabilization using microwave power as an intense source of heat to fire clays has also been considered by the Russians [27]. Power densities of 1.5 MW/m^3 would be required.

In 1982, a Japanese study basically supported these earlier findings but added some data on different types of rock and the effect of water [28]. They examined a method of breaking rocks by microwave radiation; preliminary tests were conducted with the use of 915 MHz, 100kW microwave generator. Test specimens were prepared for four kinds of rock: granite, slate, sandstone and pumice-tuff; and while radiating microwave onto them with varying moisture contents, measurements were made of the temperature rise. The thermal and breaking properties were also observed.

They concluded:

- Degree of temperature rise varies with rock type. It is greater in the sequence of slate, sandstone, pumice-tuff and granite.
- Temperature rise varies proportionally with moisture content of the specimens.
- Temperature distributions in the specimens can be classified into two groups. One is granite type, for which the temperature rise is diffuse from the surface of radiation. The other includes slate, sandstone and pumice-tuff. Temperature rise here is limited to shallow levels.
- Two patterns of rock breaking are found. One includes granite, slate and sandstone. Cracks are produced at nearly right angles to the plane of radiation. The other is the pumice-tuff type which produces a small dent, or explosion crater.

These writers also described microwave tunneling studies in areas where noise control is the governing factor. Use is limited because of the cost.

Microwave furnace designs have been considered by the Japanese; the numerical analysis methods used [29] are of considerable interest for the controlled heating of large solids, not only in radioactive waste disposal studies but also in concrete clinkering [30] and related applications. Experimental systems have been built, some having used power levels of 100 kW at 915 MHz. These may prove to be economic—or even the only solution—but so far the majority of potential applications in the area of rock and similar massives appear to be otherwise.

Shale, Tar Sand, Coal and Clays

Research into electromagnetic methods in energy (shale, heavy oil and coal) applications will provide data for developing mineral applications. Only one *collection* of articles has

been published [31]; this contains, in 10 papers, detailed technical and dielectric data on the microwave properties of sedimentary rocks, oil shale formations and coal-derived processes. A review of the methods for measuring dielectric data on rocks and shales is also given [32; in 31]. Methods for physical (scale) *modelling* of shale (tar sand) processes have been used successfully by Vermeulen *et al* [33]. This technique will be important when high temperature dielectric data are known for minerals. *In-situ* retorting of oil shales has been reviewed by Kalia [34]—similar considerations on method and choice of frequency are relevant to future mineral studies. An economic analysis for rf processing in shale oil production has been made by Mallow [35]. An analysis of the properties of pyrite, and the effect of rf or microwave conversion to pyrrhotite in coal processing, by enhanced magnetic separation, has been given recently by Bluhm *et al* [36]. A study on the effect of *caustic and microwave treatment* on clay mineral (associated with coal) has been reported by Richardson *et al* [37]. Their work is very relevant to the clay minerals under examination in this project. An abstract of their work is given below as another example of the need to consider combinations of treatment.

> Clay minerals typical of those occuring in coal (kaolinite, illite, and montmorillonite) were treated with 30 or 50% aqueous NaOH at room temperature for varying periods of time and then were either heated in a drying oven at 105°C or irradiated in a microwave unit for up to 3 minutes. The products were later washed with water or with 10% HCl. These experiments were performed to test and evaluate a chemical coal cleaning process based on reacting coal with aqueous NaOH, irradiating with microwave energy, and washing with acid to reduce the sulfur and ash content. X-ray diffraction analyses showed that no new reaction products were formed when these clay minerals were treated with NaOH solutions at room temperature. Heating in a drying oven at 105°C formed hydroxysodalite from kaolinite and a zeolite-like mineral from montmorillonite. Samples irradiated in the microwave unit underwent the greatest changes. Hydroxysodalite-hydroxycancrinite mixtures formed from kaolinite, nepheline formed from illite, and the montmorillonite dehydrated. **The results suggest that the clay minerals selectively absorbed microwave energy and were heated to temperatures above the boiling point of the solution.** The three clay minerals absorbed microwave energy to different degrees. Illite appeared to reach a higher temperature than either kaolinite or montmorillonite. The mineral products became more sodium-rich and less hydrated with increased microwave exposure time, suggesting that increasingly higher temperatures were attained. Acid washing of the treated samples resulted in the removal of all or part of the hydroxysodalite- hydroxycancrinite mixture and part of the nepheline. **Because of the significant breakdown of clay minerals during the caustic and microwave treatment, this technique is promising for the removal of ash-forming minerals from coal** [37].

Ceramics

The processing of ceramic materials with microwave heating results in uniform microstructures and controlled uniform shrinkage. In fusion research, ceramic parts of large volume and non-uniform shape have been uniformly heated (200 kW, 28 GHz) to temperatures in excess of 1600°C in both vacuum and under pressure. This uniformity of deep heating applies to many ceramic materials; the use of microwave energy in ceramic sintering offers many possibilities for a diverse set of purposes [38].

Roy *et al* [39] classify microwave applications into five sets:

> (1) Process control—used to monitor/measure parameters such as moisture, thickness, density, etc;
> (2) Drying ceramic ware, possibly the oldest application of microwave heating, used at MIT in 1949. A state-of-the-art review appeared in 1983 [40];
> (3) Use of microwave plasmas to decompose gaseous species, thereby producing highly excited electronic states of elements that combine to give metastable phases. Diamond film synthesis is the best-known example [41] (and possibly the most important—for heat sinks);
> (4) Use of microwave plasma to assist in sintering oxides without a vapour-phase material being converted to the solid state [42];
> (5) Internal heating of solid ceramics. One aspect is the sintering of ferrimagnetic materials (ferrites) in a clean, non-contact environment [43]. The other is the heating of simple, pure oxide ceramics. Ceramic - ceramic seals have also been achieved [44].

In their study, Roy *et al* [39] suggested that a critical mass exists for gels of pure SiO_2,Al_2O_3 and some silicates to heat—they used 10-20g samples in a domestic microwave oven. Their heating curves show the same tendencies as did those reported by Ford, Wong, McGill and others [45,46,17], but with more detail. These are discussed in Chapter 4.

They were unable to decipher the microwave absorption mechanism—for example, sodium ion-rattling in a cage was suggested as one mechanism by McDowell [47] for sodium nepheline. Sample size and shape in all cases studied in a multimode oven are obviously important but they are not the only factors. Electrical conductivity depends upon the orientation of crystallites, e.g., β alumina [48].

Additives have been used to increase (and control) the microwave absorption in sintering [49]—a work which provides useful general data for this study (Chapter 4) by showing the effect of 1-10% "impurities" (Si, SiC,Al) on synthetic mineral heating.

In other applications ultra-pure materials are used, e.g. fus-

ing quartz for the fabrication of optical fibres [50]. Absorption data for quartz (2.45 GHz, to 2000°C) are given in study [50] but these are difficult to interpret. Al_2O_3 - SiC whisker ceramics have also been studied, using microwave energy at 60 GHz [51]. CuO-based systems have been studied for the use of microwave energy in preparing superconducting ceramics [52]. However, all these reports lack (and complain of the lack of) high temperature dielectric and thermal conductivity data.

The overall development of the subject of microwave heating in solids (and thus chemical processing possibilities) are illustrated by the final blocks of Table 2.1. The following section defines the terms used and explains some of the physical properties involved.

Table 2.1 Historical Development: Major Process and Physical/ Chemical Data Publication Relevant to This Study

1960s	
Mineral Ore Processing - heating by microwave - tunnel applicators, - gas, liquid injection	1962/66 U.S. Patent Claims magnetite and other materials for interactive heating (susceptors, seeds) [13]
Mineral Preprocessing (in general terms)	May be disclosed by the above patent
Uranium oxide heating[a], ceramics - laboratory studies on solids in a microwave kiln to 2000°C	1967: first scientific report with comparative data, high temperature microwave ceramics, Ford [45]
Chemical/plasma research active	See, for example [53], a review
Mineral properties	At microwave: only MIT labs [54]. Limited to a few materials
1970s	
Numerous patents issued on processing specific mineral ores, and related applications[a] - continues through the '80s.	See, for example, U.S. Patents cited in the text of this report.
Mineral exploration	Unified dielectric theory [55].
Microwave heating susceptor materials for cooking	Patent activity begins ca. 1976, and continues
Metal oxides-high temperature data[a].	Wong [46];Tinga [56]
Pyrite/kaolin studies	Bodem [20]
1979 to present	
Frozen ground, de-icing[a]	Major review of theory, and Russian work [26].
Rock breaking, cracking[a] Concrete clinkering	Specialized use; in particular, inner city tunnels [23].
Analysis of mineral samples	Rapid chemical analysis, specialized small microwave ovens [57]
Grinding ores, aid to crushing	Proposed; significant efficiency improvement suggested [58]
Synthetic minerals, ceramics industry actively interested	All significant references appear in [3], the most recent collection of papers and reviews.
Properties of solids at temperatures[a]	Major area of materials science, research; increasing, see [3]above
Asphalt curing studies	Relevant for mineral properties recorded [59].
Current mineral and ore activity	
Microwave heating analysis (Laboratory Scale) - Chen et al [18][a] - U.S. Bureau of Mines [15-17,60) - Several other sources cited in text e.g. [14b,73]	
Mineral detection, analysis - Ulaby [19]	For surveying, but very important to analyzing heating properties
Ceramic material properties dielectric mixtures, heating theory[a].	See, for example, [3]
Microwave materials science[a]	Major field of research from 1982, [e.g. 39,41,43,50]
Mineral processing - Heat/detect systems	de Beers' 1987 patent cited as example [14a]

[a]Provides significant data for this study. The table's purpose is to show the linkage; it makes no attempt to present a history of microwave heating, for which the reader is referred to Osepchuk's recent and definitive work [61].

3. Microwave Heating of Solids: Definitions and Relationships

THE FOLLOWING GENERALLY ACCEPTED DEFINITIONS ARE used in this study. A **mineral** is a naturally occurring homogenous solid with a definite (but generally not fixed) chemical composition and a highly ordered atomic arrangement. It is usually formed by inorganic processes. A **synthetic mineral** is a fabricated product. **Chemicals,** such as H_2O and Hg (whether naturally occurring or not) are not minerals by definition. In this report, which is concerned to a large extent with metal oxide "impurities", the word **ore** is only used in reference to other works quoted, where data from mineral ore processing are used. The generalization **chemicals and compounds** is used for synthetic minerals in certain tables. Compositional ranges in minerals [expressed by a formula with the same atomic— generally ionic-ratios; e.g. dolomite $Ca(Mg,Fe,Mn,)(CO_3)_2$] have an implied relationship to physical data on, *for example*, the reagent grade chemical $CaCO_3$. Tables are compiled in the following sections for chemicals, compounds and minerals collectively for this reason. **Ceramics** are specific types of synthetic minerals, data from which are very relevant to this study, particularly at high temperatures. In general, ceramics are hard, brittle, (low temperature) electrical and thermal **insulators,** all of which require high-temperature processing for their manufacture. In many cases thermal conductivity decreases with increasing temperature. Many are semi-conductors at elevated temperatures, a few at 20°C. Properties which make ceramics desirable in electrical and mechanical applications are (at normal temperatures) high resistivity, high dielectric strength, controllable low dielectric and magnetic loss properties—over a wide range of dielectric constant (permittivity) values. **Oxides and ferrites** (qv) are included in this group; almost all of these are **semiconductors** above a critical temperature (T_E), a thermal runaway value which is important to this study, as it is to microwave processing in general. **Transition metal oxides,** in particular, exhibit important electronic conduction properties. [See, for example, 64:55-57.]

Thermally insulting ceramics, known as **refractories,** are of immense industrial significance; data from this area are (and will be) important to all aspects of microwave material processing. Only in a very few cases are high frequency dielectric (or heating) data known for the **rare earths.** Exceptions are fergusonite and monazite. Closely related, in a mineral context, are the data on **uranium oxides.** Rare earths were historically associated with (very) rare metals; thus, the future of mineral microwave processing, from an economic standpoint, might be associated first with this rare (and thus valuable) family of materials.

Pyroelectricity and piezoelectric minerals may also be important in this subject area. There are, to the best of the writer's knowledge, no high temperature, high frequency data available relevant to heating effects (i.e. loss mechanisms). If, for example, quartz is heated above 100°C, on cooling it will develop positive charges at three alternative prismatic edges and negative charges at the remaining three. In practice, all

microwave absorption mechanisms above 100°C in quartz will be affected by bound water, some of which is not released below 900°C. **Ferromagnetic materials** of primary interest here (as common minerals and as impurities) are magnetite (Fe_3O_4) and pyrrhotite $Fe_{1-x}S$.* Magnetite is a natural **ferrite**, of which all ferrites, as a group, are considered "derivatives". Ferrites are often termed **ferrospinels** because their crystal structure is similar to the mineral spinel ($MgAl_2O_4$). From a microwave absorption viewpoint, there are two overlapping families of materials here: (a) oxides and metal sulphides, carbides and bromides, which have *no* appreciable magnetic effects; and (b) the ferrospirels, which become **paramagnetic** above the Curie temperature T_c (for pure magnetite T_c ~ 585°C and for magnetic iron T_c = 770°C). At high temperatures (>150°C) only the electric and magnetic properties of magnetite are known in the microwave spectrum—and then they are controversial because of their complexity due to the non-linearities at T_c and the conversion rate (to hematite) above and below T_c.

Magnetite is one of the strongest microwave **susceptors** (absorbers) known, after UO_2 and ultra-thin films of certain metals (e.g. Al at ~ 100Å.**). In all cases material absorption is critically determined not only by purity and density (particle size), and water content (bound and free—often in impurities) but by thickness (electrical size). In terms of relative susceptibility to heating, these materials are followed by certain (transition) metal oxides, sulphides, bromides, carbon and carbides. Carbon (graphite) properties are known to be very sensitive to particle size. This hyperactive family of susceptors (which are common, and therefore critical impurities), are also called microwave **interactive (heating) materials** and **thermals seeds.** The mineral magnetite, in practice, contains other oxides which are themselves susceptors.

The electromagnetic properties of all susceptors other than metal films have to be analyzed statistically. This work began in the 1970's; only in 1988 have statistical data on rocks appeared which are relevant to microwave heating studies, and then only at 25°C [19]. Density, particle shape and size all affect the dielectric properties. **Mesh size** (in extractive mineralogy) is either a positive or negative number. The material which passes is undersize (negative number), oversize is recorded as a positive number. These numbers do not relate directly to density or density distributions in many cases, which makes the interpretation of some literature values difficult.

Microwave definitions and material properties are given in the following paragraphs. The average power absorbed by a material per unit volume (P_A) is proportional to the loss factor (ε'') and the square of the electric field strength (E_{rms}) within the material at an angular frequency ω (=$2\pi f$)

$$P_A = \omega \varepsilon_o \epsilon'' E_{rms}^2 [W/m^2] \qquad (1)$$

where ε_0 is the permittivity of free space and ε'' is the loss factor. ε'' is the effective value due to all loss mechanisms, discussed in the following paragraphs. If a magnetic material is involved, equation (1) must include magnetic wall domain and electron spin losses: μ'' is again an effective total value which includes eddy current losses, in terms of the magnetic field strength (H):

$$P_A = \omega \epsilon_o \epsilon'' E_{rms}^2 + \omega \mu_o \mu'' H_{rms}^2 \qquad (2)$$

Equations 1 and 2 are discussed by Metaxas and Meredith [6:70-89] who provide a clear overall derivation of microwave heat and mass transfer relationships.

The penetration depth (D_p) is defined as the distance (z) from the surface of the material (z=0) at which the power transmitted into the material drops to 1/e of its value at that inner surface: $P_A \alpha \exp[-2\alpha z]$ where α is the attenutation factor [Np/m] and

$$D_p = 1/2\alpha \qquad (3)$$

which has been plotted in detail for foods [6:74-77,81]; and for certain rocks and minerals [26]. Although equations (1-3) are complex, and require a detailed knowledge of ε',ε'', $\mu'\mu''$ (ω,T)—particularly in the cases involving mixtures—they have been extensively analyzed. Heat and mass transfer studies exist in, for example, drying sandstone [62].

Equation 1 illustrates an apparent microwave versus rf advantage: as the frequency increases, E decreases for a given P_A; however, D_p decreases with increasing frequency. For these, and additional reasons associated with large tunnels and cavities, 915 MHz is often the best compromise frequency for processing large materials of irregular shape. In tunnels at 915 MHz, P_A and the selectivity associated with a P_A offer greater design flexibility for many drying and curing applications.

In practice, experimental data on overall loss mechanisms are fitted to empirical relations, all of which have a sound physical basis involving many types of interaction. For solids, a general expression takes the form [63;6:19-25]

$$\epsilon''\{\omega, T\} = \epsilon_o B\{T\} \omega^{n\{T\}-1} \qquad (4)$$

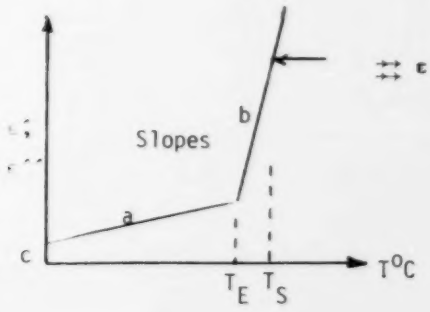
where B(T),n(T) are temperature dependent parameters.

More detailed expressions, and their derivations or empirical reasons, are given for solid dielectrics by Bartnikas in an ASTM Technical Publication [64]. However, simple empirical models for solids at microwave frequencies and high temperatures do not appear to have been developed. Based on a survey of the literature at both low (rf) frequencies and a limited microwave data base, we suggest one here, which is illustrated

* Most pyrrhotites have a deficiency of iron with respect to sulphur: in general $0 < x < 0.2$, an omission solid solution.

** Metal films at this thickness form connected "islands"; the behaviour of metal (and metal oxide) "flakes" and particles isolated in ceramics gives rise to the term "thermal seed".

in Figures 3.1 and 3.2. In piece-wise linear approximation ε'' (T), and in most cases ε' (T), take the form shown in equation 5.



$$\varepsilon = \begin{cases} aT + c, \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots T \leq T_E \\ (aT_E + c) + (b(T - T_E)), \ldots\ldots\ldots\ldots T > T_E \end{cases}$$

a, b, c, T_E are constants at a particular frequency; T_S see text.

(5)

where T_E is the "breakpoint"—at the knee of the original curve (Figure 3.1) At $T < T_E$ some materials have a more complex response (Figure 3.2), illustrating both the "hard to heat" and "thermal runaway" cases (see, for example, the tables in 18). Further, a **field exclusion temperature** (T_S) occurs above which value the surface reflection (due to ε'; $D_p \to 0$) limits the heating process. T_S is thus, in practice, a function of insulation and power density, which is a possible explanation for the effects observed and discussed by Tinga [56], Wong [46], McGill [17], and first observed by Ford [45]. All the parameters (a, b, T_E, T_S) are frequency dependent. With a few exceptions data available to date allow only their estimation at 2,450 MHz but not at 915 MHz. Many different loss mechanisms can occur in any one particular material; an example is the zeolite family [65]. Their economic importance as both natural and synthetic minerals justifies a detailed study [66].

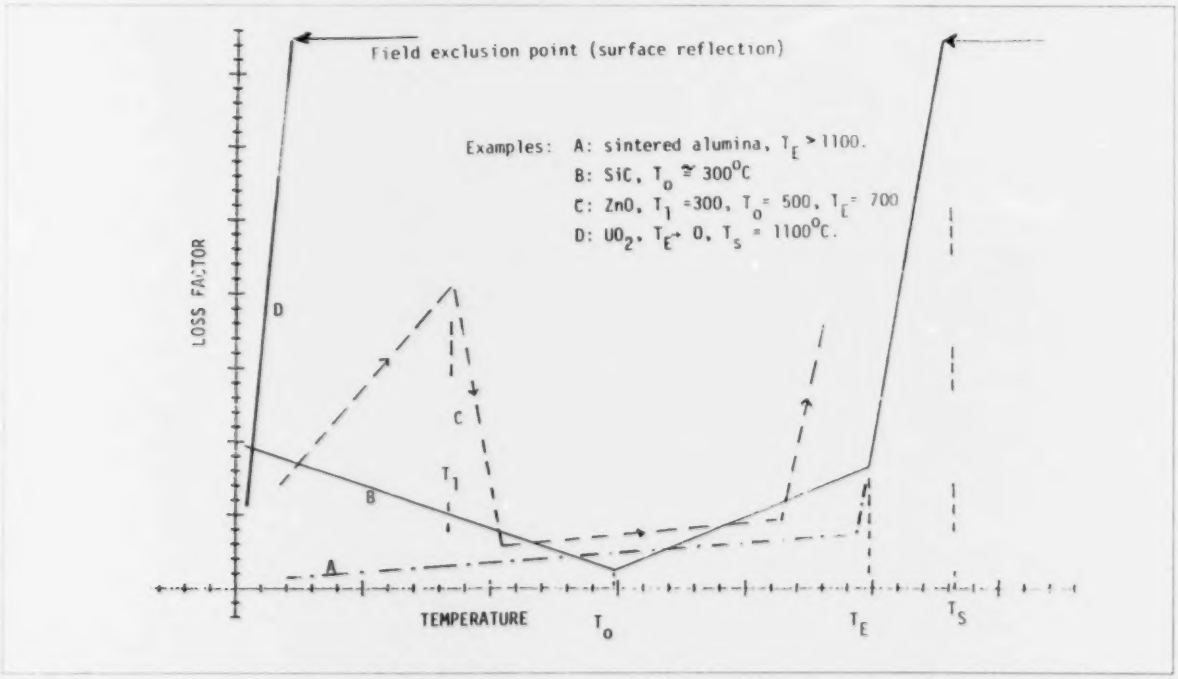


Figure 3.1
Illustrating the loss factor trends for many ceramics and minerals in piece-wise linear approximation.
Values quoted are from the literature; in most cases from single samples, at 2,450 MHz. One family, the zeolites, may encompass all the cases shown.

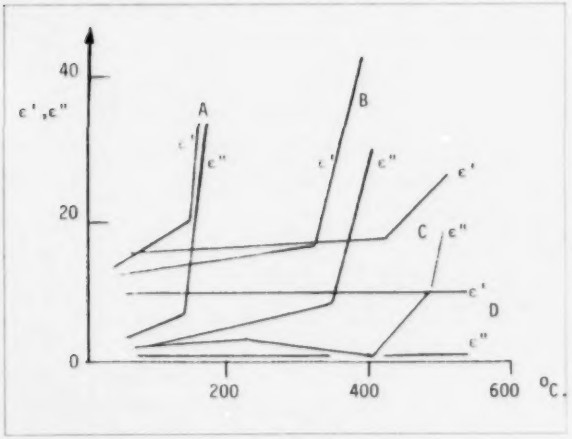


Figure 3.2
Dielectric data for four sulphide minerals and ores at 2,375 MHz (90). A: pyrrhotite, $Fe_{1-x}S$ (where x lies between 0 and 0.2 as most pyrrhotites have a deficiency of Fe with respect to S); B: chalcopyrite, $CuFeS_2$; C: pyrite, FeS_2 and D: sphalerite, ZnS. Original data were almost linear to these lines shown. Relative heating rates reported correspond to these values.

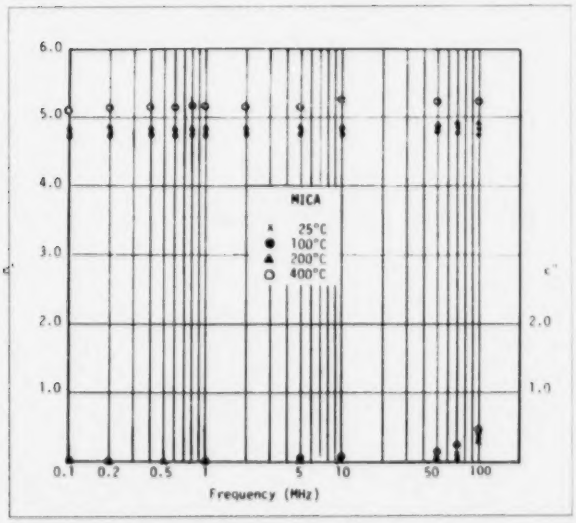


Figure 3.3 Complex permittivity of mica as a function of temperature, to 100 MHz (33).

We illustrate the dielectric parameters discussed above with some relevant literature values. Hoekstra [26], Vermeulen [33] and others [*in* 31] have calculated some useful relative dielectric values for rocks, oil sands, clays and minerals. These can be used as a guide, a general illustration. All values are at 20°C.

Clay (silty clay soil),	15% water content (g H_2O/g soil)
ε':10, ε'':5	mid 10^9 - 10^{10}Hz band
Soil, shales, schists;	above 15% water content
$1 < \varepsilon'' < 10$	10^9 - 10^{11}Hz; mainly due to water
Granites, Basalts	
$0.1 < \varepsilon'' < 1$	10^9 - 10^{11}Hz; high density, low water content
Hard rock	
$D_p \sim 1$m	10^9Hz
Soft rock	
$D_p \sim 0.05$m	10^9Hz
Oilsand	
5.6% H_2O content	
$D_p \sim 0.2$m;	
1.3% H_2O content	
$D_p \sim 1$m	both at 10^9Hz

Two specific cases of ε', ε'' are illustrated. The values for mica (Figure 3.3) show a small increase with increasing temperature above 50 MHz. Bound water is believed to affect the loss mechanism up to temperatures as high as 600°C. The values for the ceramic MgO are illustrated in Figure 3.4 and suggest that T_E ~800°C, which is similar to the value for magnesium aluminum silicate (Figure 3.5). The frequency dependence of T_E is not known.

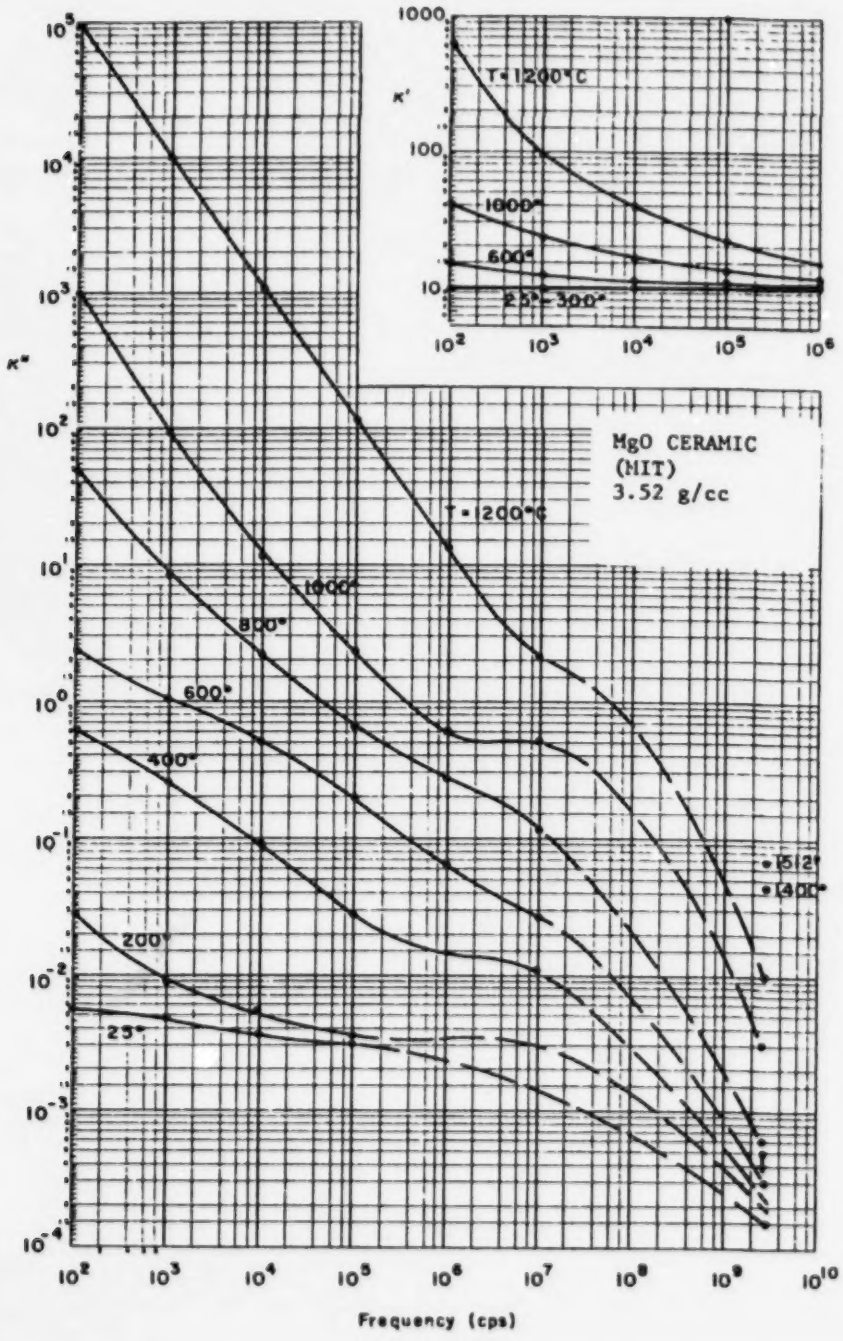


Figure 3.4
MgO ceramic (54). A few materials which have important microwave communications/accelerator applications have been analyzed into the low microwave spectrum at high temperatures. Generally these are high T_E materials. In this case both a and b (Equation 5) are small to 1512°C with the T_E value ~ 800°C at 1 GHz.

Non-thermal and **thermal-specific (narrow band)** loss effects have been suggested by Roussy et al [67,68] in studying both zeolites and fluorite (CaF_2) flotation processes under electromagnetic radiation. In their model [68] they relate the local (internal) value of the electric field E_i to the power absorbed. One interpretation is a field interaction effect resulting in a very high value of ε'' for a water saturated zeolite or a fluorite solution under certain conditions. ε'' (T) is known to be a complex, high-valued function for some zeolites [65] and for simple ionic crystals (e.g. ZnS,CaF_2), as well as valence-2 metals with valence-6 atoms (e.g. ZnS,ZnO), which are semiconductors by definition [69:32]. Dissolved ionic solids respond to electric fields, exhibiting high conductivities. The effects of water of crystallization and bound water can add to the complexity—two more dielectric absorption mechanisms, together with ion exchange mechanisms [70]. Non-thermal effects are unlikely; however, micro-thermal interactions are possible.

Mixed valence energy level transitions have been suggested as the loss mechanism for UO_{3-x} [11]. For the absorptions found in certain calcium silicates and aluminates, Komarneni and Roy [65] have suggested a model based on ionic motion in a cage: the zeolite framework is sufficiently open to accommodate water along with other molecules and cations. The evidence so far suggests that there is a strong structural (framework topology) dependence on the loss mechanism in certain zeolites but not in their mineral forms. Mineral silicates and aluminates (clays) do not have cations of sufficient mobility, it is thought, in the required framework (cage) locations to respond to the microwave energy at low temperatures. At high temperatures crystalline and non-crystalline forms do respond—all, possibly, in a fashion represented by Figure 3.2. Data in the following section illustrate some of these effects in terms of microwave heating experiments reported in the literature.

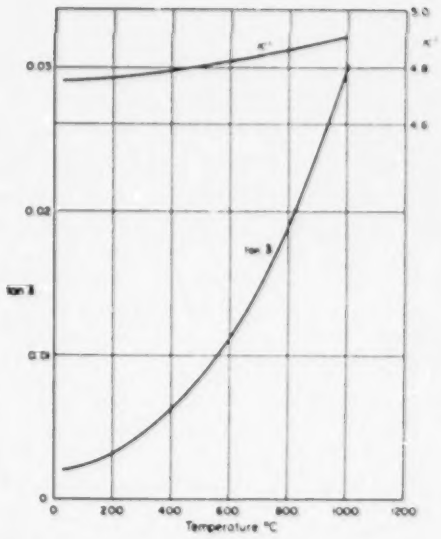


Figure 3.5
Magnesium aluminum silicate; Cordierite ceramic, at 9.52 GHz; Density 2.44 g/cm³.
Here k' is the dielectric constant ε'; tan $\delta = \varepsilon''/\varepsilon'$ (54)

4. Microwave Heating Studies on Rocks and Minerals

In 1967 Ford and Pei [45] studied high temperature chemical processing by microwave heating in a resonant, 2.45 GHz cavity. They heated oxides and sulphides to temperatures < 1900°C using cavity power levels up to 1600 W. They observed that, in general, dark coloured compounds heated rapidly to a cut-off temperature near 1000°C, whereas light coloured materials required a longer time but reached higher temperatures (Table 4.1). The first sintering data appear in their study [45].

Table 4.1
Heating rates recorded by Ford and Pei, 1967 (45) at 2.45 GHz in a resonant cavity. Sample sizes varied from 10g (dark materials) to a 200g (light materials). (B) signifies a violent reaction; in the case of MnO_2, the reaction could not be recorded.

Compound	Colour	Heating Time (min)	Max.Temp (°C)
Al_2O_3	White	24	1900
C (Charcoal)	Black	0.2	1000
CaO	White	40	200
Co_2O_3	Black	3 (B)	900
CuO	Black	4	800
CuS	Dark blue	5	600
Fe_2O_3	Red	6	1000
Fe_3O_4	Black	0.5	500
FeS	Black	6	800
MgO	White	40	1300
MnO_2	Black	(B)	—
MoO_3	Pale green	46	750
MoS_2	Black	0.1	900
Ni_2O_3	Black	3 (B)	1300
PbO	Yellow	13	900
TiO_2	White	—	—
UO_2	Dark green	0.1	1100
ZnO	White	4	1100

They were also the first to suggest that the cut-off temperature (T_S) is due to surface relection of microwave power, a self-limiting effect for heating discussed in the previous section. This is illustrated in Figure 4.1 for UO_2 and CuO. The results follow the models in Figure 3.2. In a carefully designed waveguide reactor they studied the sintering of UO_2 pellets. They suggested that a considerable reduction in heating and cooling time was possible with microwave sintering; a factor of four is suggested by their results, all in agreement with recent reports [3].

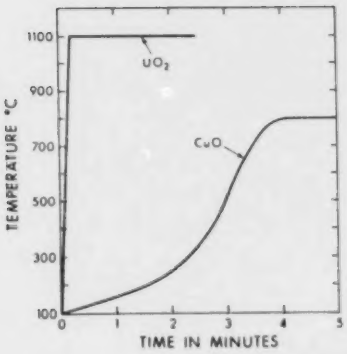


Figure 4.1 Relative heating rates (2.45GHz) for UO_2 and CuO (From 45).

These ideas were pursued by Wong [46] in 1975, working with Tinga over several years [56]. They measured the high temperature properties of specific oxides in a microwave cavity (reflection and heating rate) and also under slow conduction heating. Their results for CuO, shown in Figure 4.2, agree with the earlier work [45]. Table 4.2 compiles these with other data to illustrate the range of cavity heating rates and attempts a classification of material activity. Wong also provided essential dielectric data on reagent grade materials (Figures 4.3 and 4.4) which explain the different heating rates. Wong's work [46] provides valuable detail as well on microwave cavity design and has been quoted by a number of subsequent researchers. His bridge circuit is shown in Figure 4.4A, the insulated waveguide cavity in Figure 4.4B.

In 1984 Chen *et al* [18] reported microwave heating data on 40 mineral samples using a 2.45 GHz resonant cavity. Their apparatus, simpler than Wong's [46], is shown in Figure 4.5. Their objective was to ascertain the general behaviour of minerals in air under small-sample heating conditions.

Table 4.2
Microwave heating rates (at 2.45GHz): a compilation of comparable values, from data reported (45,46,56). Reagent grade materials. Heating conditions similar but not identical.

Material Classification	Heating rate reported	Maximum Temperature (°C)	Reference and Notes
(a) Hyperactive Materials			
	~°C/s		Note that these
UO_2	200	1100	materials tend to black, with high
MoS_2	150	900	thermal
C (Charcoal)	100	1000	conductivities.
Fe_3O_4	20[a]	500/1000	See ahead for mixtures of Fe_3O_4/Fe_2O_3
FeS_2	20	500	
CuCl	20	450	
MnO_2	—	—	Probably >20°C/s [45]
(b) Active	~°C/min		
Ni_2O_3	400	1300	Violent
Co_2O_3	300	900	Violent
CuO	200	800	
Fe_2O_3	170	1000	
FeS	135	800	
CuS	120	600	
(c) Difficult to heat			See also tables ahead
	~°C/min		
Al_2O_3	80	1900	Type unspecified
PbO	70	900	
MgO	33	1300	
ZnO	25	1100	
MoO_3	15	750	
(d) Inactive	~°C/min		See also tables ahead
CaO	5	200	
$CaCO_3$	5	130	
SiO_2	2-5	70	

[a]dT/dt probably large enough to mask oxidation effects.

They concluded that:

- most silicates, carbonates and sulphates, some oxides and some sulphides are transparent to microwave radiation (Table 4.3);
- both natural and synthetic jarosite-type compounds are unaffected by microwave radiation;
- most sulphides, arsenides, sulphosalts and sulphurarsenides are readily heated and consequently fuse or dissociate prior to eventual oxidation (Table 4.4);
- a number of oxides heat rapidly.

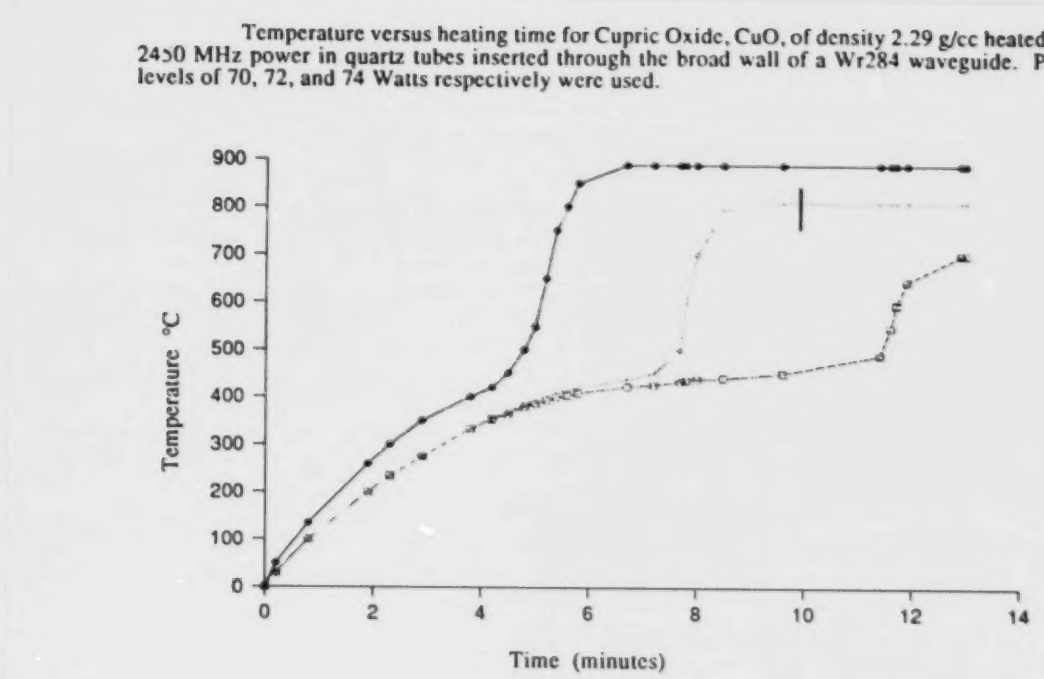


Figure 4.2
CuO heating at 2.45 GHz. With permission of the publishers of Electromagnetic Energy Reviews. (From 46, 56)

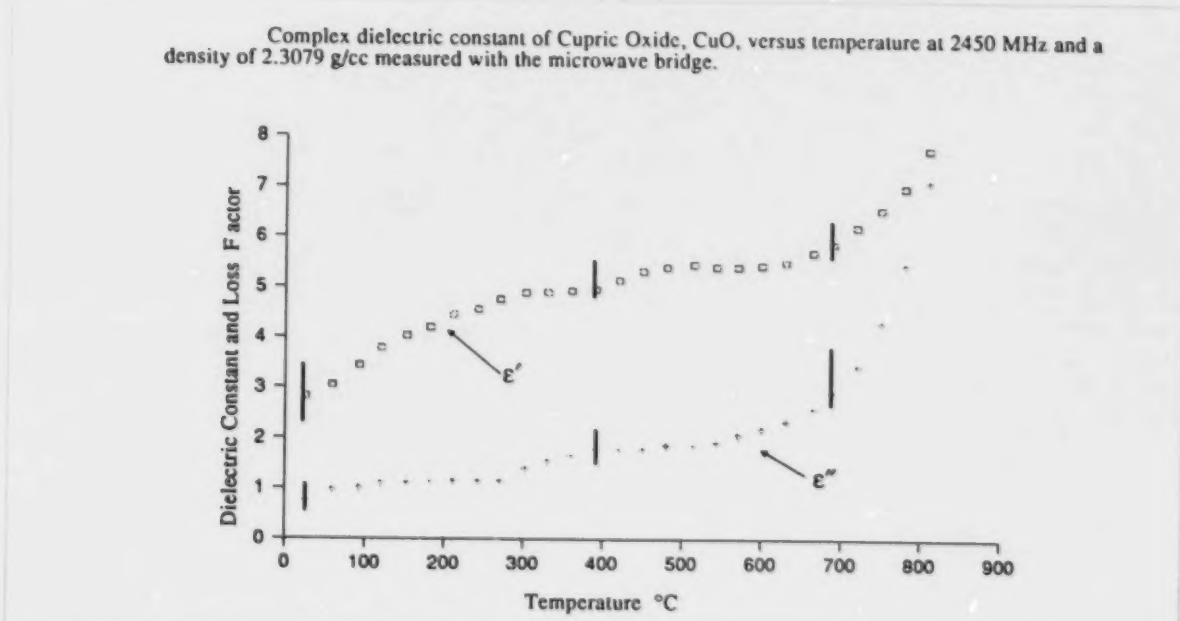


Figure 4.3
CuO dielectric data, from (56).

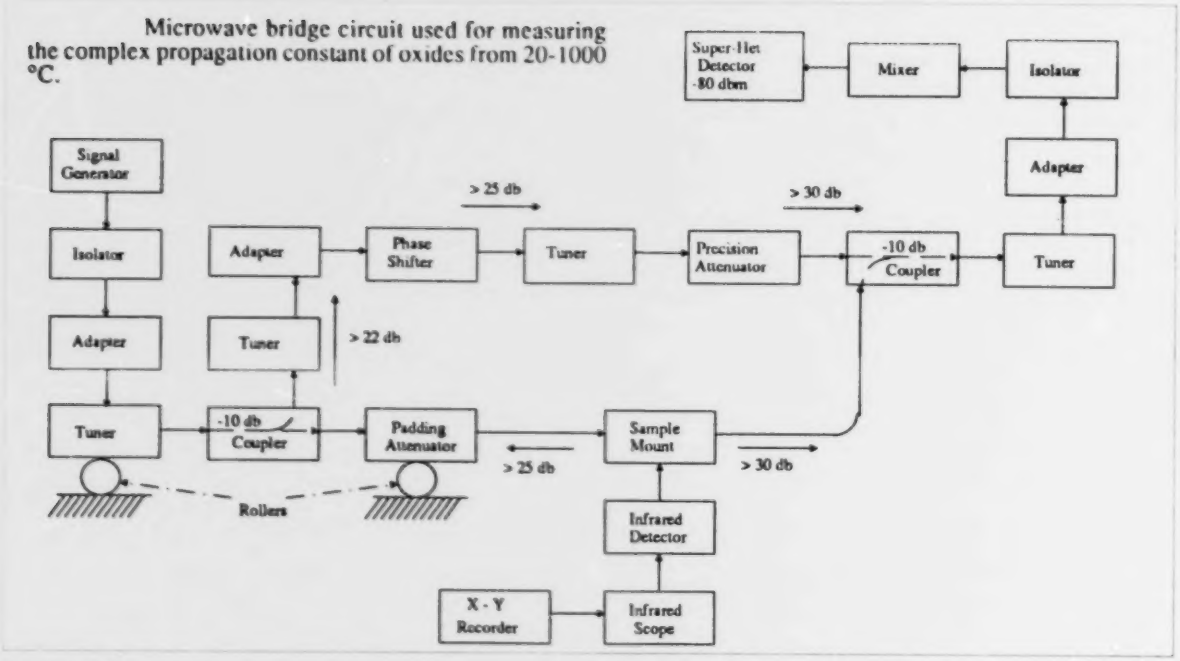


Figure 4.4A
Microwave dielectric bridge circuit (56).

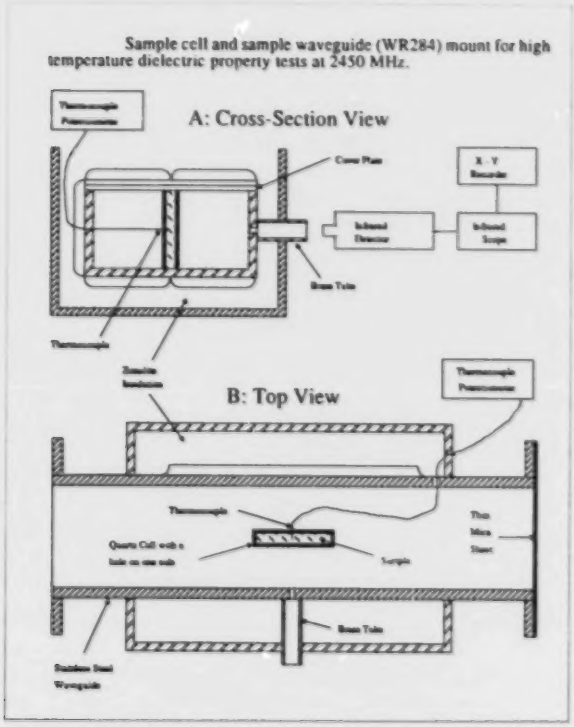


Figure 4.4B
Sample cell for microwave bridge circuit.(56)

They observed that microwave heating effects are largely determined by composition and elemental substitutions. Tables 4.2 - 4.4 are consistent, suggesting that mineral heating can be predicted in a general fashion from tests on major chemical constituents.

The results of Chen *et al* [18] represent a major contribution to study of microwave-mineral ore behaviour because they made heating observations *and* performed chemical analysis before and after heating. For this reason their results are given in full in Tables 4.3 - 4.5.

They made the following observations [18]. First, the heating results fell into two categories:

(a) No, or very little, heating, due to transparency *or* surface reflection at room temperature; mineral properties unaltered.

(b) Heat is generated and the minerals will either remain thermally stable or dissociate/react rapidly.

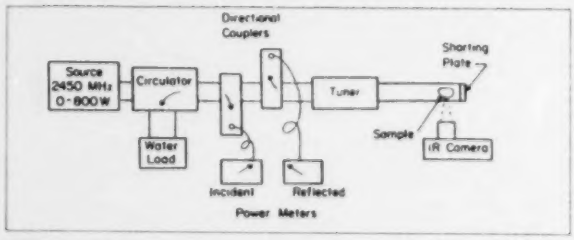


Figure 4.5
Microwave cavity system for mineral sample heating(18).

Table 4.3
Minerals transparent to microwave irradiation: microwave frequency 2,450 MHz; power 150W; exposure 5 min. (18)

Mineral Class	Minerals/Compounds
Carbonates	Aragonite, calcite, dolomite, siderite
Jarosite-type compounds	Argentojarosite, synthetic natrojarosite (zinc plant residue, Kidd Creek Mines Ltd), synthetic plumbojarosite (zinc plant residue, Cominco Ltd)
Silicates	Almandine, allanite, anorthite, gadolinite, muscovite, potassium feldspar, quartz, titanite, zircon
Sulfates	Barite, gypsum
Others	Fergusonite, monazite, sphalerite (low Fe), stibnite

Table 4.4
Results of microwave heating experiments on ore minerals; microwave frequency 2,450 MHz; exposure 3-5 min.(18)

Mineral	Power (W)	Heating Response	Product Examination
Arsenopyrite	80	Heats, some sparking	S and As fumes; some fusion. Pyrrhotite, As, Fe-arsenide and arsenopyrite
Bornite	20	Heats readily	Some changed to bornite-chalcopyrite-digenite; some unchanged
Chalcopyrite	15	Heats readily with emission of sulfur fumes	Two Cu-Fe-sulfides or pyrite and Cu-Fe-sulfide
Covellite/anilite (60% vol. %)	100	Difficult to heat; sulfur fumes emitted	Sintered to single composition of $(Cu, Fe)_9S_5$
Galena	30	Heats readily with much arcing	Sintered mass of galena
Nickeline/cobaltite (3 vol. %)	100	Difficult to heat	Some fused; most unaffected
Pyrite	30	Heats readily; emission of sulfur fumes	Pyrrhotite and S fumes
Pyrrhotite	50	Heats readily with arcing at high temperature	Some fused; most unaffected
Sphalerite (high Fe; Zn 58.9, Fe 7.4, S 33.7%)	100	Difficult to heat when cold	converted to wurtzite
Sphalerite (low Fe; Zn67.1, Fe0.2, S32.7%)	>100	Does not heat	No change, sphalerite
Stibnite	>100	Does not heat	No change; stibnite
Tennantite (Cu 42.8, Ag 0.1, Fe 4.8, Zn1.7, As 12.5, Sb 10.6, S 27.5%) (90 vol. % tennantite, 6% chalcopyrite, 4% quartz)	100	Difficult to heat when cold	Fused mass of tennanite-chalcopyrite; arsenic fumes emitted
Tetrahedrite (Cu 24.9, Ag18.0, Fe 1.9, Zn 4.8, Sb 25.6, As 1.3, S 23.4%) (85 vol.% tetrahedrite, 10% quartz, 5% pyrargyrite, galena, chalcopyrite)	35	Heats readily	Fused mass of Ag-Sb alloy, PbS, tetrahedrite, Cu-Fe-Zn sulfide and Cu-Fe-Pb sulfide

Secondly, mineral deposits of jarosite-type materials could not, apparently, be decomposed *in situ*. Thirdly, that composition is critically important to heating rate (i.e. Fe - Zn substitution) and (by implication) oxides and sulphides of metals (in particular Fe) in small, or localized concentrations were equally important. Thus, one could, in principle, be separated from gangue by microwave heating.

Table 4.5
Results of microwave heating experiments on oxides and uranium minerals: microwave frequency 2,450 MHz; exposure 3-5 min. (18)

Mineral	Power (W)	Heating Response	Product Examination
Allanite	>150	Does not heat	No change; allanite
Cassiterite	40	Heats readily	No change; cassiterite
Columbite (40 vol%) - pyrochlore in silicates (almandine 40%)	60	Difficult to heat when cold	Niobium minerals fused; most silicates unchanged
Fergusonite	>150	Does not heat	No change; fergusonite
Hematite	50	Heats readily; arcing at high temperature	No change; hematite
Magnetite	30	Heats readily	No change; magnetite
Monazite	>150	Does not heat	No change; monazite
Pitchblende (90 vol.%) contains chlorite, galena, calcite	50	Heats readily	Some fused to UO_2,U_3O_8, ThO_2 and Fe-Al-Ca-SiO_2 glass; others unchanged.

Recently the U.S. Bureau of Mines has reported data on the microwave heating characteristics of selected minerals and compounds [15,16,17,58,60]. They used 2.45 GHz microwave ovens and waveguide heating systems in these studies. Extractive applications and stress fracturing at normal grain boundaries were discussed [15], suggesting a new process for reducing grinding energy requirements. But this was concluded to be not cost effective [58], with the proviso that a combination of improved grindability and cleaner liberation might give rise to viable new processes. Collectively, as they state, insufficient tests have been done to date to analyze the economics; however their data are impressive. Surprisingly, they ignored (in one case dismissed) the earlier work [18,46,45].

In an extractive metallurgy report [16], McGill *et al* showed that certain valuable minerals (galena, ilmenite, magnetite and chalcopyrite) are heated whereas host rock minerals (quartz, calcite and felspar) are not. Some of their relative heating rates are shown in Table 4.6 for high purity natural minerals; these relate to tests in a commercial microwave oven with small 25g samples alongside a 1 litre water load (see note to Table 4.6).

Table 4.6
Relative heating rates, high purity, at 2.45 GHz (16)[a]

Rapid heating (>300°C/min)	Active (~100°C/min)	Slow (10-20°C/min)	
Chalcopyrite ($CuFeS_2$)	Chalcocite (Cu_2S)	Albite	Arizonite
	Galena (PbS)	Chromite	Cinnabar
Magnetite (Fe_3O_4)	Pyrite (FeS_2)	Hematite	Marble
Pyrrhotite ($Fe_{1-x}S$)		Molybdenite	Orpiment
		Orthoclase	Quartz
		Sphalerite	Tetrahedrite
		Zircon	

[a]These data are only comparable to those from other methods (e.g. 18,45,46,56) in rank (relative position in each table) *not* in heating rate values due to the different heating systems used. Microwave oven data on small samples are, at best, indicative of heating rates. Additional data are given in the following tables.

They also reported heating rates on 54 reagent grade elements and compounds [15]. A method is described to produce a magnetic phase on pyrite surfaces, to retort cinnabar (by the addition of 20% magnetite) and for the roast-leaching treatment of chalcopyrite ore, similar to the methods taught by an earlier U.S. patent [13].

Of particular interest to this study are the data given by McGill in another paper [17]. Here the effect of incident microwave power level on the heating rate of some oxides, sulphides and chlorides are given. There is some disagreement between McGill [17] and Wong [46] with the latter using a more elaborate technique which may have reduced heat losses. Table 4.7A summarizes the results. Results of the type given in Table 4.7A clearly emphasize the need for further study on the effect of reaction rate. A partial explanation of rate effects may have been given by Hu [71].

Table 4.7A
Relative heating responses according to (17); waveguide system.

Material	Cut-off temperature (field exclusion) T_S [°C]	Response
Fe_3O_4	~1100	Very rapid. Independent of power level
FeS_2	~ 700	Very rapid. Some dependence on power level.
CuCl	—	Rapid; cut-off only apparent at lowest power level (450°C)
Cr_2O_3	—	Rapid. No apparent cut-off at 1400°C.
ZnO	300?	Slow, <1/10th of CuCl,1/20th of Fe_3O_4
SiO_2	—	Slow,<1/100th of CuCl
$CaCO_3$	—	Slow, similar to SiO_2

Surface heat loss effects and different power coupling factors make comparisons of the work in the literature extremely difficult at this stage. For this reason tables have not been combined. However, clear trends emerge. In general an increase in incident power increases the heating rate, except for very low loss materials (SiO_2, $CaCO_3$) and very high loss ones (UO_2, Fe_3O_4, FeS_2, CuCl etc). *Sensitivity to power level lies with the intermediate-range materials;* there is no disagreement on this important point.

We illustrate the effect of power level on heating rate in a mixture test which was performed during the course of this study—Table 4.7B. Reagent grades of Fe_3O_4,Fe_2O_3 were used; increasing the proportion of Fe_2O_3 reduces the heating rate (1.2 kW microwave oven, Ceraform™ insulation 14g layer samples) from 740°C/min to 12°C/min. As a comparison we took 300g samples of Fe_3O_4 (a layer 8.8^2 x 6.7 cm in Ceraform) and investigated the T_E values and rates **under these conditions,** obtaining quite different results: (a) and (b) in Table 4.7B.

Table 4.7B
Sample heating tests; 1.2kW commercial microwave oven with heavy insulation (see text).

(a) 14g total weight % Fe_2O_3/Fe_3O_4	Heating rate °C/min (in the first minute)
0/100	740
70/30	300
80/20	150
90/10	70
100/0	12 [150°C in next 10 minutes]
(b) 300g sample Fe_2O_3	100 [to 550°C]
	500 [~550 - 1150°C in 2nd minute]
Fe_3O_4	~1000 [in first minute]

Table 4.8
Relative heating rates of rock and mineral referred to water; 300g samples in a 650 W microwave oven (From 59 and our data)

Material	Rate °C/min
Diorite	112
	100,47*
Gabbro	88
Granulite	65,46*
Amphibolite	64
Aplite	58,106*
Granite	58,39*
Biotite	43
Limestone	42,5*
Schist	36,5
Sandstone	33,36*,8.4*
Pyrrhotite	26,5,41*
Water	**24**
Gneiss	22,5
Quartzite	8,5

* See Figure 4.8

A road maintenance study [59] provides some comparative data on microwave heating rates for the rocks and minerals listed in Table 4.8 from Figure 4.8. Baillot [59] compared his 2.45 GHz results to the heating of the same volume of water in the microwave oven. Although this comparison has no real meaning either—the dielectric constant of water is typically one order of magnitude above that of the other materials heated and thus the electrical length of the samples and their coupling to the microwave fields are different—it does allow, on a relative or rank basis, the inclusion of other values. For a pilot test on this point we obtained samples of biotite, limestone, and pyrrhotite. We repeated the procedure used by Baillot [59] in one of our 650W microwave ovens, normalizing all of the values to a 300 mL water load heating rate. Our relative data agreed, for limestone, to within 20% so we have added our two minerals to his ranking of relative heating rates in Table 4.8. We also changed the volume of water used and, as expected, obtained completely different rates, which is the strongest argument for dismissing all measurements, in terms of absolute heating rate, made in a multimode resonant microwave oven, particularly small domestic and commercial models. *However, relative values still show a consistent trend.* The effect of layer (sample) thickness on heating rate in a microwave oven has been analyzed theroetically and experimentally by Jain [72]. Dimension changes alone in a sample can alter actual heating rates in an oven by more than 2:1. Thus, the hyperactive materials will be recognized by all oven tests—in support of this argument the relative values in the previous tables agree, in their ranking, with the accurate (for small samples) cavity results obtained by Chen [18], Wong [46] and Ford [45]. Pyrrhotite has not been examined scientifically; we suspect from the above that it has a high dielectric constant but absorbs rapidly above 100°C; sandstone and limestone show the effect of drying in Figure 4.8.

There are two areas of development where microwave ovens have been re-designed for sample heating, making them into scientific systems. One is very effective and is finding significant use in mineral sample analysis [57]. The other is in the study of certain synthetic zeolites in which comparisons were made with some clay minerals [65].

Mineral sample analysis by microwave heating

The U.S. Bureau of Mines has developed a microwave heating method for dissolving ores, slags, furnace products and ashes rapidly in acid for atomic absorption analysis and other instrumental techniques [57]. The method is rapid (~10s heating time) and considered both reliable (Table 4.9) and cost-effective. An earlier report [73] suggested the use of the microwave and acid inert material polycarbonate for the sealed container in a 1.5 kW laboratory microwave oven. CO_2 was used then to cool the sample containers and remove acid fumes. Teflon is more suitable for containment of various acid combustions and the durability is acceptable—with more than

75 dissolutions possible. Samples prepared by this method can be analyzed for elements at major, minor and trace levels of concentration from a simple solution. The elements include Si, Al, Ca, Mg, Fe, Cu, Mn, Ni, Co, Na, K with an accuracy comparable to conventional dissolution methods. A 1987 patent [U.S. 4,693,867]describes a commercial system using the same basic technique, together with a transporting system which takes each sample container to a **controlled** microwave heating zone in individual, random and automatic succession. A sample extraction system is included. A waveguide heating chamber is used, allowing for the precise, individual treatment of each 10-20 mL sample. Although the cavity (microwave oven) method has been used extensively for sample analysis (in particular, drying fuel samples), waveguide techniques are preferable, giving greater repeatability between samples. Microwave plasma heaters, and thawing systems for frozen cells, use very similar waveguide chambers—either in a travelling wave (as in this case) or resonant configurations.

Zeolites

The very high heating rates reported for specific zeolites [65] are of great interest to the ceramics industry and possibly to mineral flotation processes [67, 68]. The specific microwave absorption mechanisms postulated for these alumino-silicates have not been reported in any other mineral study. At this stage we can only quote their results (Table 4.10) and note their conclusions [65]:

- clay minerals such as montmorillonites which have no dielectric channels or cavities, did not melt, even though these layer silicates exhibit cation exchange behaviour;
- microwave absorption behaviour of zeolites is a function of the location as well as mobility of the cations within the zeolite framework;
- gels, in particular aluminosilicate gels, which are non-crystalline, can be melted—but require a higher temperature to start the process [11].

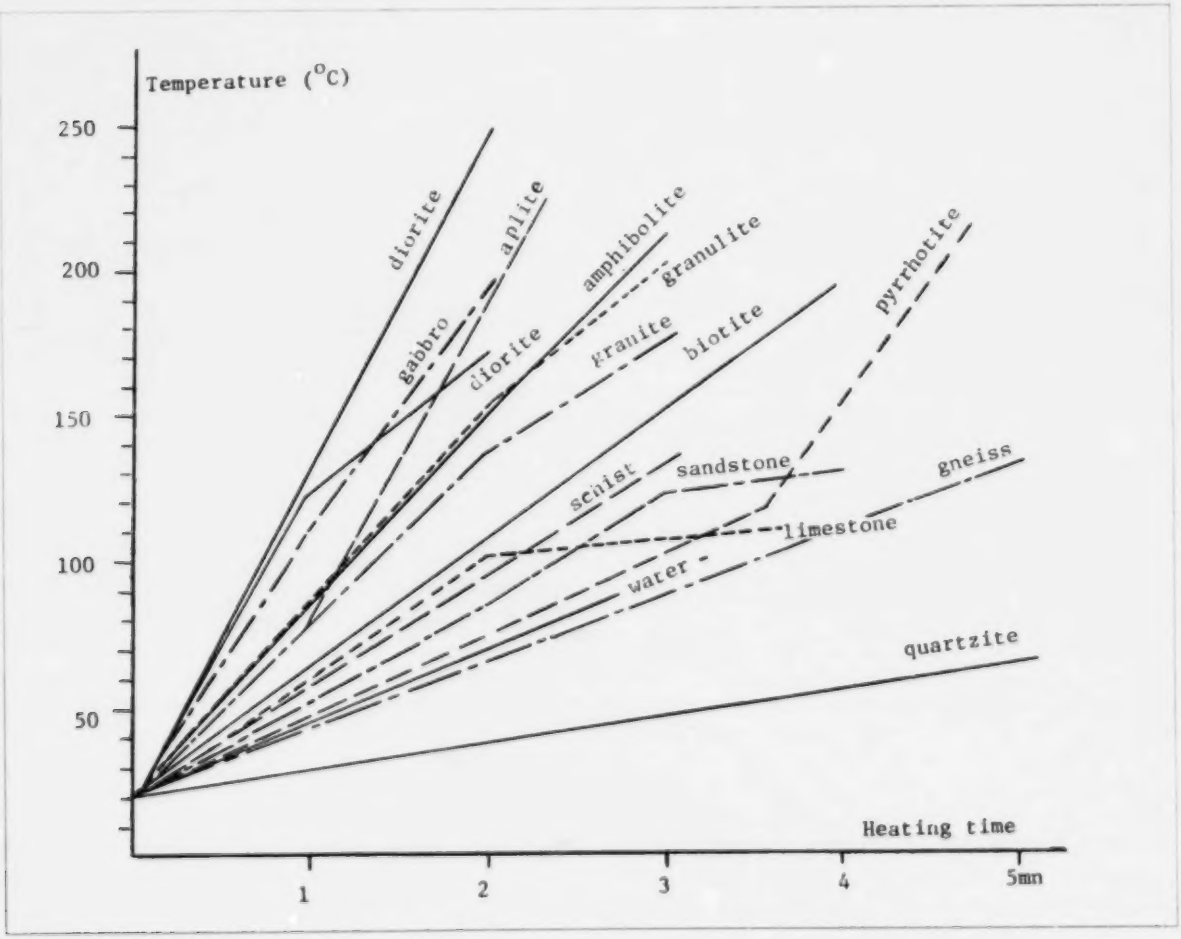


Figure 4.8
Relative heating rates for minerals and rocks at 2.45 GHz (From 59 and other tests—see text)

Table 4.9
(From 57) Comparisons of various dissolution techniques, percent

	Fe	Si	Mn	Ca	Mg	Al	Ti	Na	K
CANADIAN ORES									
SY-2									
Certified or verified value	4.4	28.1	0.25	5.7	1.6	6.4	NA[a]	3.1	3.5
Microwave and Teflon	4.4	28.1	.28	5.7	1.6	6.6	NA	3.5	3.2
Parr bomb	4.5	26.6	.27	5.6	1.5	5.6	NA	2.7	3.3
Polycarbonate bottle	4.8	28.3	.30	5.4	1.6	7.4	NA	3.1	3.4
Fusion	4.4	27.5	.21	5.8	1.6	6.0	NA	NA	3.5
SWEDISH SLAG									
NO. 7									
Certified or verified value	14.5	9.6	4.1	31.5	4.0	1.1	0.20	NA	NA
Microwave and Teflon	14.8	9.7	4.1	31.2	4.1	1.2	.22	NA	NA
Parr bomb	14.7	9.3	4.3	32.3	3.9	.83	.16	NA	NA
Polycarbonate bottle	14.9	9.6	4.1	31.6	4.4	1.1	NA	NA	NA
Fusion	14.7	9.5	4.0	32.4	4.1	1.1	.23	NA	NA
LABORATORY REFERENCE STANDARD SINTER 101									
Certified or verified value	54.9	3.6	0.46	7.4	1.2	0.76	NA	NA	NA
Microwave and Teflon	54.8	3.6	.47	7.4	1.2	.77	NA	(0.05)[b]	NA
Parr bomb	53.1	3.5	.49	8.6	1.2	.89	NA	(.06)	NA
Polycarbonate bottle	55.0	3.8	.56	7.3	1.2	.72	NA	NA	NA
Fusion	54.6	3.6	.46	7.5	1.1	.78	NA	NA	NA
LABORATORY REFERENCE STANDARD COAL ASH 524									
Certified or verified value	6.9	23.3	NA	1.9	0.43	15.9	0.78	0.36	1.1
Microwave and Teflon	7.0	23.4	NA	1.9	.43	16.0	.78	.37	1.2
Parr bomb	6.8	21.8	NA	2.0	.42	11.8	.76	.46	1.1
Polycarbonate bottle	7.1	23.3	NA	1.8	.43	15.4	.76	NA	NA
Fusion	7.3	23.7	NA	2.1	.43	16.2	.80	NA	1.3

[a] NA Not analyzed

[b] Numbers in parentheses were determined, but the sample had no certified value for the element.

The three zeolite minerals in Table 4.10 which did melt—i.e. their heating rate appears to be close to that of susceptor (thermal seed) materials—merit detailed study, in particular high temperature dielectric and chemical change analysis.

Additives

The addition of 1-5% Al or 1-10% SiC has been shown to alter the heating rate of inert (high T_E) mineral particles to a significant extent [49] - possibly the only detailed report of its type in the literature. In this patent other additives (metal oxides) are also considered. Figure 4.9 (a) shows the heating rates of pyrophyllite/zircon in comparison to sintered alumina, synthetic mullite, MgO and Si_3N_4. Figure 4.9 (b) shows the rates for Si (of two mesh sizes), graphite, SiC and Cr_2O_3. The addition of 1-10% of SiC to the pyrophyllite 40%/zircon 60% mineral is shown in Figure 4.9 (c). A 1% addition of SiC increases the heating rate by more than 10 times; apparently 1% is almost as effective as 10%. Strangely, we can find no verification of this result elsewhere, neither is there any reference to it in the other literature quoted. SiC is not, theoretically, the most likely thermal seed; indeed its reported data [54] suggest it is not a low temperature interactive material, due to the dip in the ε" versus T response at ~ 150°C. However, mesh size may be a critical parameter (see inset upper curves in Figure 4.9).

Table 4.10
2.4 GHz Heating of Zeolites, Alumino (tecto)-silicates (40) [ab]

Group	Rapid heating/ melting	No melting
Analcime		x
Pollucite		x
Heulandite		
Clinoptilolite	x	
Phillipsite	x	
Mordenite		x
Chabazite		x
Erionite	x	
Sodalite		x
Faujasite		
Zeolite A (4A, Na^+form)	xx	
Zeolite A	x(slow)	
(3A, K^+Na mixed cation form)		
Zeolite A		x
(5A, Ca+Na mixed cation form)		
X (13X, no cation form)	xx	
Albite		x
K-feldspar		x
Montmorillonite, Na and Ca		x

[a] No other comparative data found

[b] For an excellent explanation of the classification of zeolites and their structure (cages,frameworks) see Barrer,R.M. *Zeolites and Clay Minerals as Solvents and Molecular Sieves*, 1978, Academic Press NY:16-30 and their Table 1. The ionic physics is discussed by Beam [69].

Comparative heating rates

We have found only one comparison of microwave heating rates at 915 versus 2,450 MHz —in the European patent literature [14b]. This patent describes a process for the recovery of metals from host materials by preferential absorption of microwave energy. Sulphidic and oxidic compounds are converted to other compounds (such as oxides and chlorides) from which the metal is more readily recoverable. It is suggested that copper, molybdenum and rhenium ores can be treated in this way. Sixteen examples are given in [14b]; Table 4.11 has been compiled from two of these which gave data at both frequencies under almost the same conditions. It is apparent that 2,450 MHz is far more "selective", suggesting that T_E occurs at a much lower temperature, or the loss factor is initially far greater (below T_E) at the higher frequency for some sulphides, one oxide and a silicate. No other values can be found in the literature to support the result, which may be significant in some mineral pre-processing considerations.

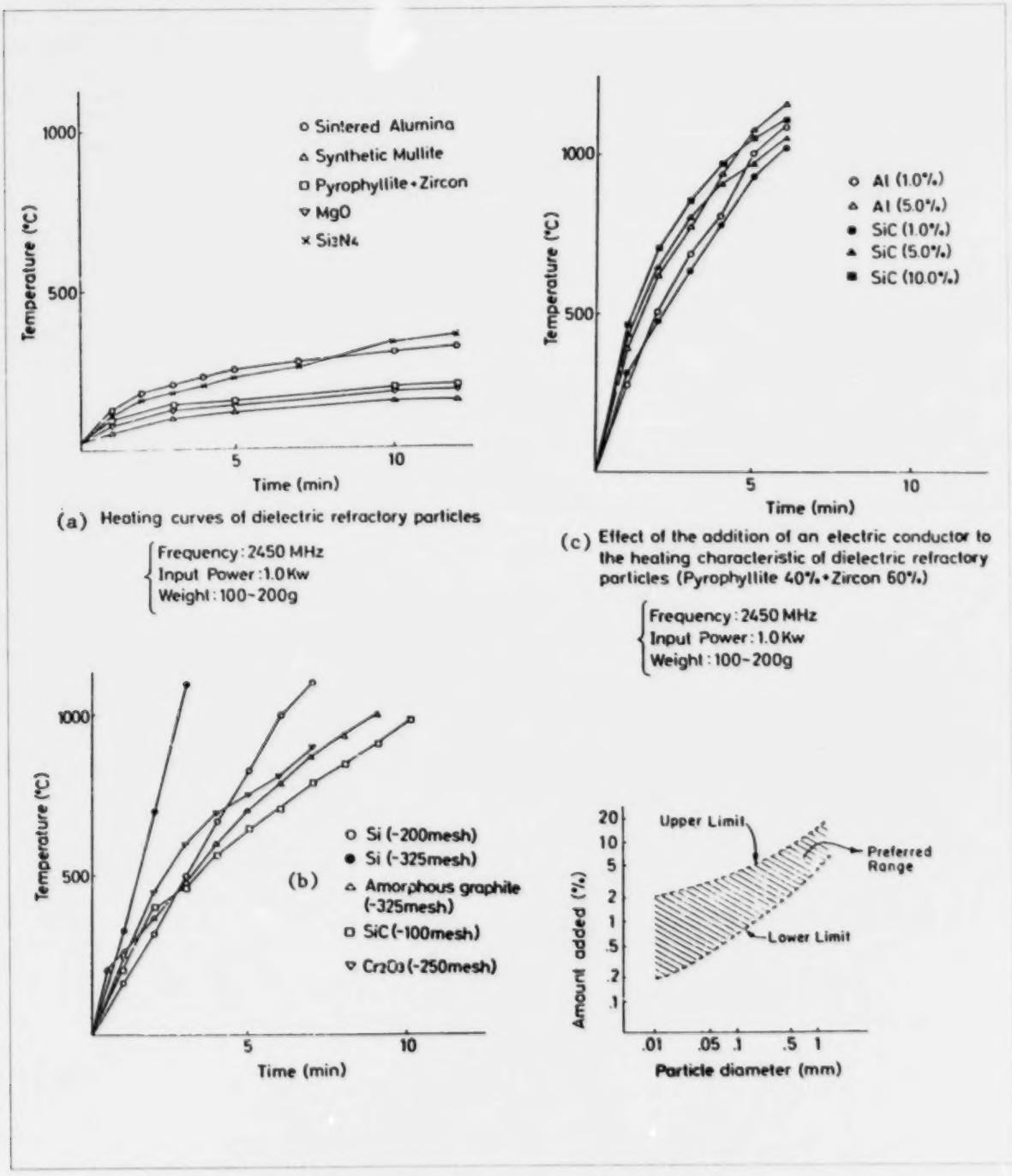


Figure 4.9
Heating rates for refractories, additives and in combination, at 2,450 MHz and 1 kW. (a) 100-200 g samples of refractories, (b) 200-300 g samples—three possible additives and (c) two additives, percentage by weight shown—in (pyrophyllite 40% + zircon 60%) ($Al_2Si_4O_{10}(OH)_2/ZrSiO_4$). (From U.S. Patent 4,147,911 1979-Method for Sintering Refractories, 49).

Summary

From the data discussed here in terms of Equation 5 in Chapter 3, it is suggested that:

- a, b, and the exciting (critical) temperature T_E (Figure 3.4) are constants for each material, all of which are expected to depend on structural factors (density, particle size etc.) as well as frequency;
- a cut-off temperature (T_S) may occur due to surface reflection—a field exclusion effect which limits (regulates) the final temperature;
- T_E is small for susceptors and thermal seeds, in the main metal oxides, sulphides and bromides—with notable exceptions (see Tables);
- T_E is large (up to 2000 °C) for other common materials, which include silica. *Critical parameters in determining the other parameters may be dT/dt and/or $P_A E_i$.*
- The effect of impurites (low T_E materials) on host minerals cannot be determined in any detail from the heating data available.

Table 4.11 Comparative heating rates at 915 and 2,450 MHz under comparable conditions for small (25g) samples with 250-300W cavity input power (From EPA 0-041-841, 1981).

Material	Temperature (°C) after 6 minutes of heating	
	915MHz	2,450MHz
Sand	29	36
Iron Oxide (FeO)	28	34
Sphalerite	34	34
Zinc Oxide	29	38
Cupric Oxide	70	195
Chalcopyrite $CuFeS_2$	58	324
Bornite Cu_5FeS_4	73	>600
Chalcocite Cu_2S	42	124
Chrysocolla $(Cu_4H_4Si_4O_{10}(OH)_8)$	46	108
Covellite (CuS)	79	244

In the case of magnetite it is reasonable to postulate that the actual value of T_E is determined by the oxidation rate and the incident energy density—due to the existence of a Curie temperature at which value the total absorption changes. This is illustrated in Figure 4.10. Other materials may show a more complicated response with both frequency and temperature. The predominant mechanism is, or is similar to, that of a semiconductor in all cases: each material becomes a complex microwave semi-conductor above a critical temperature.

We examine next the microwave dielectric effects of "impurities" in rocks and the effect of low T_E additives on these host materials.

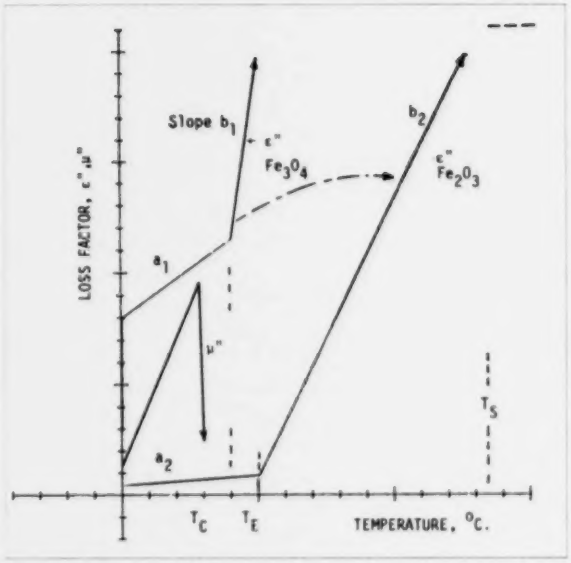


Figure 4.10
Postulated temperature response, for Fe_3O_4 - Fe_2O_3 in piece-wise linear form at 2,450 MHz. T_C is the Curie temperature for Fe_3O_4 (~575°C) above which $\mu'' = 0$. At a temperature just above this ε'' shows a runaway effect. In the presence of oxygen, Fe_3O_4 changes to Fe_2O_3 above 200°C. Fe_2O_3, which is non-magnetic, has an ε'' response of the form shown, where T_E, for one reagent grade sample, was found to be 650 ± 50°C. The dashes indicate the probability of a field exclusion temperature T_S due to surface reflections when ε' becomes very large. Values in practice depend on particle size and reaction rate (74).

5. Dielectric Data on Minerals

ALL WRITERS ON MICROWAVE MINERAL AND CERAMIC PROcessing have regretted the absence of high temperature dielectric data. The heating data (previous section) clearly indicate that, for minerals, each has to be measured and considered separately, with statistical data determined from many samples and related to their constituents.

In this respect the dielectric work of Ulaby *et al* [19] is particularly important: they measured properties over a range of microwave frequencies in terms of loss factors for constituents of rocks but (because of their geophysical interests) only at room temperature.*

Ulaby *et al's* low power measurement system is shown in Figure 5.1. This method can be used for accurate *in-situ* measurements or with test cavities. The probes, based on an extensive number of designs and evaluations in the literature [quoted in 19] are shown in Figure 5.2**. Although expensive, the system is fast, accurate and versatile; it is becoming the standard method. (Adaptions are needed at high temperatures—see Chapter 6). Reference (known) materials are used for calibration: over a 20 GHz band width, the deviation is $<\pm 2\%$ in Ulaby's case. One application (an example of the sensitivity of the microwave method) is illustrated in Figure 5.3.

Ulaby *et al* [19] used a combination of these techniques to investigate the dielectric properties of 80 rock samples in terms of bulk density in the microwave region 0.5 - 18 GHz; for 56 samples they measured the bulk chemical composition. They concluded that:

- the dielectric constant, or permittivity, ε' is frequency independent in this range and shows the greatest variation for silicates (Figure 5.4); $\varepsilon'<9$ in all cases;
- the bulk density, ρ, accounts for ~50% of the variance in ε' [Figure 5.5];
- for individual rock types (by genesis), ~90% of the observed variance may be explained by a combination of density and the fractional contents of **SiO_2,Fe_2O_3***,MgO,TiO_2;**
- for the loss factor, ε'', statistically significant relationships with density and chemical content did not occur. However, their data are significant from a potential heating view point.

* We thank Dr. Ulaby and his colleagues, and the University of Michigan Ann Arbor, for permission to reproduce data and figures from their report, Reference 19, in this chapter.

** A detailed description and analysis of low power, normal temperature microwave property measurement systems with references can be found in [32], with examples of their use in [31].

*** The chemical analysis method in this case does not distinguish between Fe_3O_4, Fe_2O_3 and FeO.

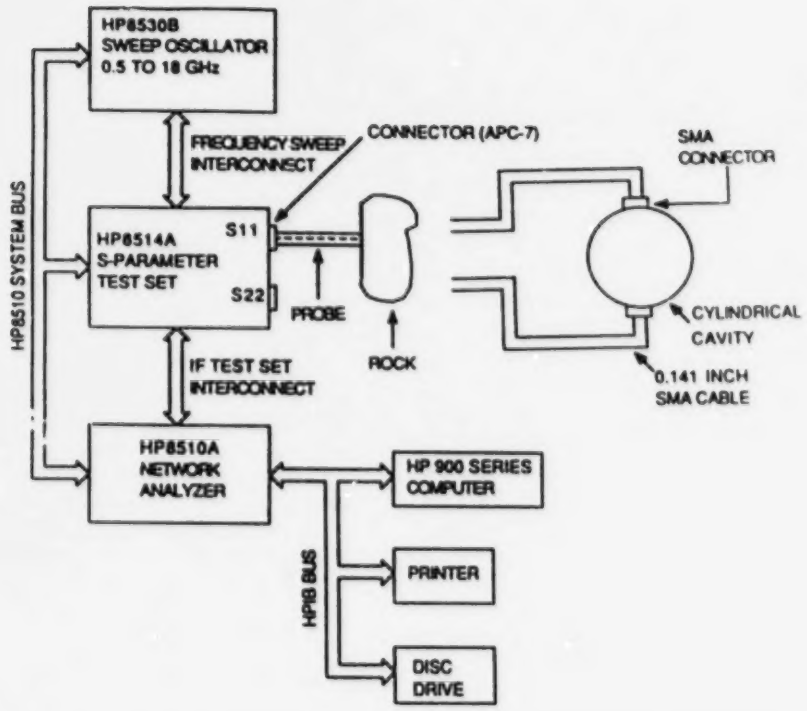


Figure 5.1
Block diagrams of the system used by Ulaby *et al.* (19). Either direct contact can be made to a thick sample or a cavity technique can be used. See also (75) for design details and theory.

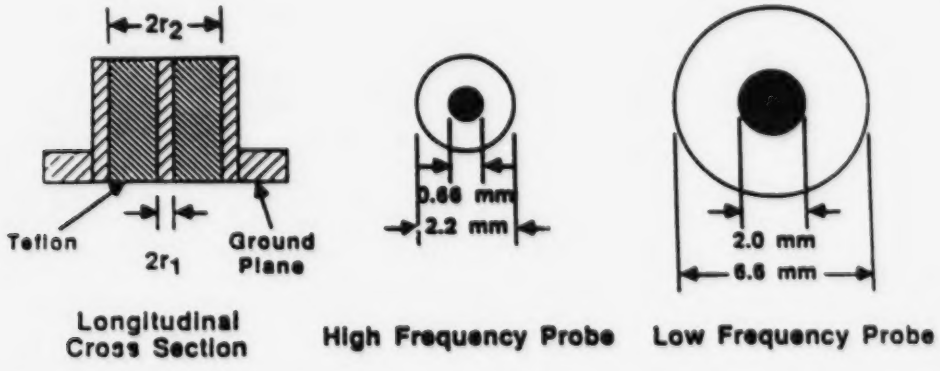


Figure 5.2
Dielectric non-penetrating probe; in the case of mineral and rock analysis, requires one flat surface and sufficient thickness to avoid far-surface reflection errors. Often an artificial "pad" can be used.

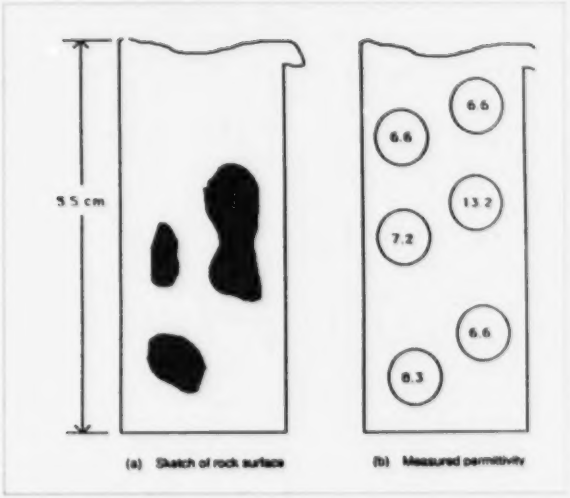


Figure 5.3
Sample detection—due to Ulaby *et al* (19). The dark areas (a) are high iron content, related to the dielectric measurements (b).

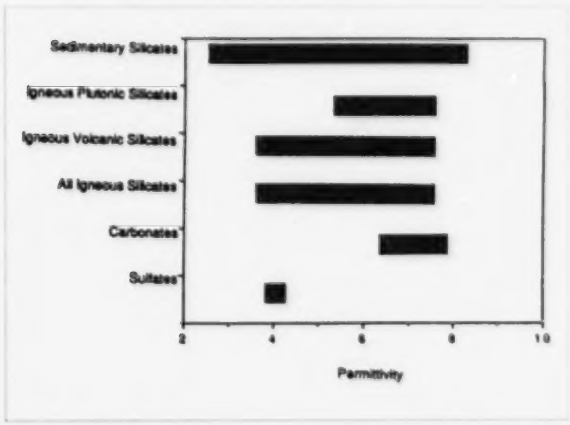


Figure 5.4
Range of ε' for individual rock types (19).

For silicates, their predicted relationship for ε' takes the form shown in Figure 5.6, where the multipliers (MgO, etc.) are the percentages by weight of each constituent. Density appears there also as a multiplier; by itself they determine the relationship to be 1.96 raised to the power ρ. If all silicates are included in one expression, the ε' relationship becomes more complex but the predicted value is very close, R = 0.88 (Figure 5.7).

Loss factor (ε") data for all rocks tested in [19] are shown in Figure 5.8 by individual types; and versus frequency in Figure 5.9. A pattern emerges (albeit weakly) between these (accurate) data and those shown in Figure 4.8 on a relative basis. Figures 5.8, 5.9 are significant in terms of mineral families and provide a start for a future analysis on frequency

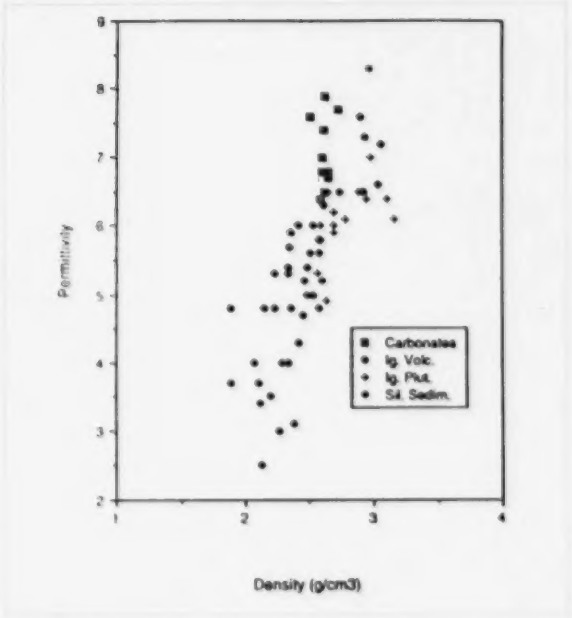


Figure 5.5
ε' versus density for individual rock types (19).

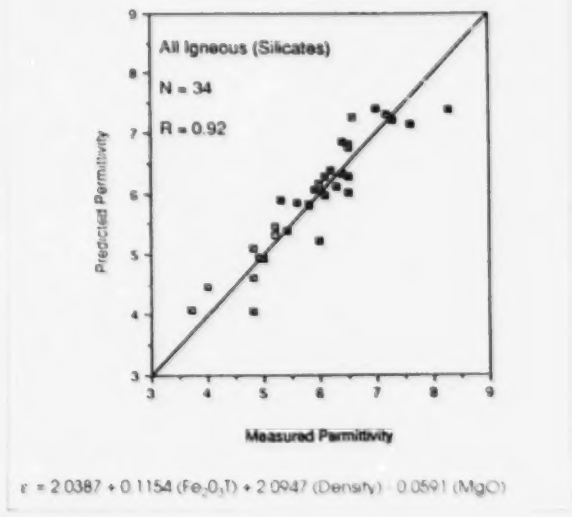


Figure 5.6
Computed ε' versus measured for all igneous rocks (19).

selection (915 versus 2450 MHz) for processing. Silicate ε" values, and their prediction (Figure 5.10) defy analysis except that key "impurities" are identified: from an examination of the tabulated data [19], 2:1 changes in iron oxide content appear to have a significant effect on ε" in all cases.

A systematic approach to the description of electrical parameters of rocks was put forward in 1970 by Fuller and Ward [55]. This strong theoretical base has been developed in the last two decades, with significant contributions from Sen and Chew [see, 31:95-106].

Recently Thorp and Rad have published rf and microwave data at high temperatures on Ca, Fe and Mn oxides and silicides, in the majority of cases for single crystals, with detailed discussions [76-81]. They have added considerable information on the dielectric data of materials which are constituents of minerals. Their work merits a detailed analysis in terms of dielectric models at high temperatures, a study which is beyond the scope of this project.

We consider next some specific minerals and rocks about which some dielectric observations can be made: **talc, quartz, basalt, salt and obsidian.** Parkhomenko [82:200-240] has reviewed the dielectric data on minerals and rocks at frequencies $<10^7$ Hz. Temperature and frequency dependence of the dielectric values are known for only a few minerals above 0.1 GHz [54]. Collectively, [54,82] show the trends at higher frequencies. Quartz and talc, for example, have been studied extensively below 10^7 Hz; the data are reviewed in detail in [82]. The effect of different types of bound water is considered to be the major loss mechanism, which is significant at temperatures up to 600°C *according to the dielectric literature**. In muscovite, water evolves on heating between 300-400°C, but most is released in the range 600-700°C. These "states" have been recognized from dielectric measurements below 10^6 Hz. Micas are known to emit rf noise at very high temperatures which may, again, involve bound water. Talc may also exhibit distinct temperature ranges where bound water becomes "free". Absorption "peaks" are thought to be due, in order of increasing temperature, to:

- Polar OH group rotation, or of molecules of water of crystallization;
- Transitions from water of crystallization to free water;
- Other structural changes relating to water of crystallization or lattice (cage) effects.

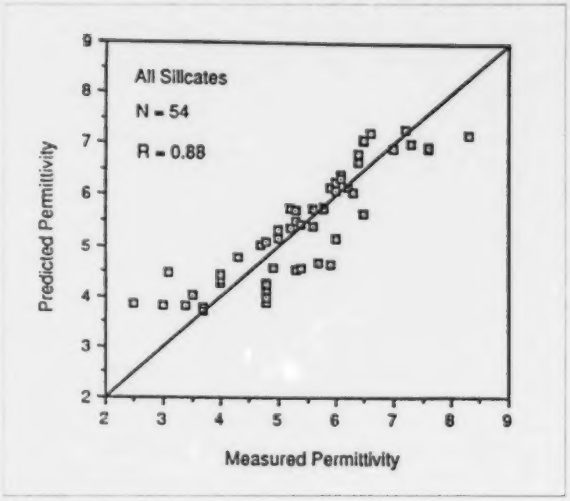


Figure 5.7
Prediction of ε' for all silicates (19).

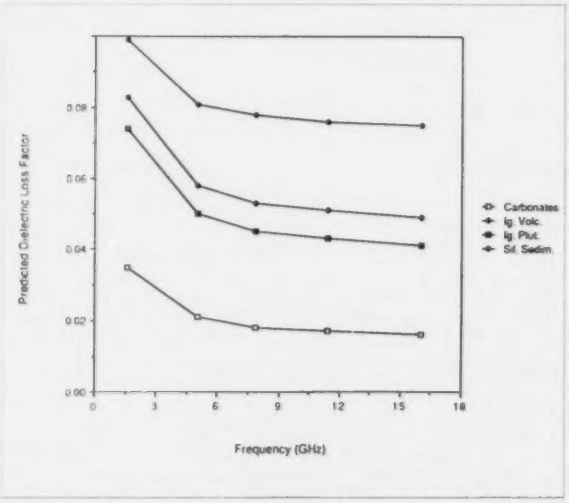


Figure 5.8
Spectral variation of ε'' for individual rock types (19).

* Here a difficulty is apparent, one which we have detected in other cases. Dielectric data are usually recorded with slow, intermittent convective heating, so water may be released, or reordered, at different apparent temperatures. Talc, an acid metasilicate of magnesium is $H_2Mg_3(SiO_3)_4$ or $H_2O.3MgO.4SiO_2$ = Silica 63.4, magnesia 31.7, water 4.8 = 100. With normal heating, one half of this water is said to be lost below dull red-heat, the remainder rapidly at ca 900°C [Dana's Mineralogy]—and there is no disagreement on this. However, the water content can vary considerably and Ni is sometimes present, as are dielectrically unknown impurities, including chlorite (silicates of Al with ferrous iron and Mg, and chemically bound water, together with several ion exchange possibilities.) Dielectric loss mechanisms of almost all types are thus possible and may depend critically on dT/dt.

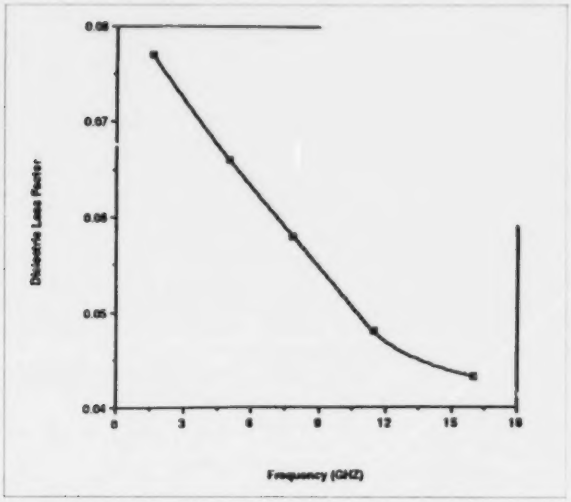


Figure 5.9
Average ε" for all rock samples (19).

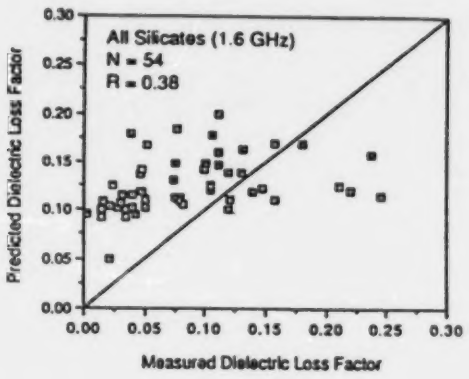
An equally likely explanation is an impurity which becomes active at high temperatures, possibly in combination with water molecules.

In a pilot test we heated solid 250-500g talc and mica samples in a 1 kW microwave oven, roughly equivalent to Baillot's method [59]. The surface temperature of the talc sample rose to ~ 400°C after 12 minutes; after 18 minutes cracks appeared, with an internal temperature estimated to be 700 ± 50°C. No other reaction was observed. The muscovite mica sample heated less, to 150°C in 20 minutes (~6.5°C/min), less than even one quartzite sample (Figure 4.8).

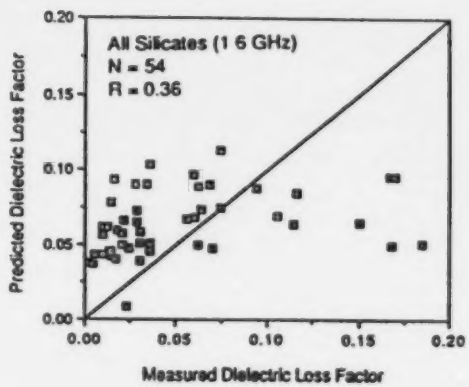
These were all single samples (indeed *no* report which we have found contains multiple location/sample heating). This particular muscovite sample contained layers of a light yellowish-brown material in the cleavage planes, presumed to be an iron oxide from the mineral form of αFeO.OH (goethite) or $FeO.OH.nH_2O$ (limonite), and/or an oxide of tin. This merely emphasizes the need for chemical analysis.

There are reports of both talc and obsidian being processed by microwave energy. In the latter case it has been verbally stated by second-hand sources [83] that obsidian is exported from Idaho to Japan where it is "processed" into aggregate for concrete—an unlikely application as glasses are not generally used in concrete. The loss factor for obsidian at 25°C differs by more than 2:1 for different samples [19]; a greater than 10:1 variation is theoretically possible in any case where significant concentration distributions, layers or pockets of a susceptor material occur in a mineral [84]; see also, for glasses, [64:56-57].

A range of samples, with a full analysis, is obviously required before any conclusions can be drawn. However, small variations in bound water also have to be measured; these are known to make a very significant absorption difference in, for



(a) 1.6 GHz



(b) 16 GHz

$$\varepsilon'' = P_1 + P_2/f;$$

P_1 = 0.2224 – 0.0019(SiO2) – 0.0040(K2O) – 0.0026(MgO) – 0.0062(Na2O) – 0.0180(MnO)

P_2 = –0.0381 + 0.0027(Fe2O3T) – 0.0772(P2O5) + 0.0037(Al2O3) - (0.0053) + 0.0007(AlO2)

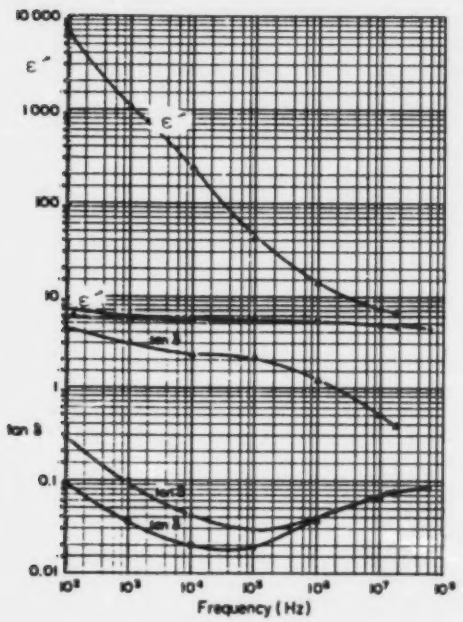
Figure 5.10
Predicted versus measured dielectric loss factor for all silicate rock samples analyzed (19).

example, low density Hawaiian basalt*—more than one order of magnitude for the final 2% of water at 1 MHz [54]. The trend, however, is for this difference to disappear at high (microwave) frequencies (Figure 5.11), which is theoretically reasonable.

Some chloride pastes have been studied—as susceptors in the food industry. Microwave data are available [72]; the val-

* Basalt is the volcanic equivalent of gabbro: dark, fine-grained. It contains feldspar and may contain natural glasses.

Hawaian low-density basalt



- % H_2O on dry weight basis 0.441
  % H_2O on dry volume basis 0.0617
  density 1.401 g/cm^3
- Dry (after 3 days in oven at 105°C
  density 1.400 g/cm^3
- % H_2O on dry weight basis 2.71
  % H_2O on dry volume basis 3.79
  density 1.438 g/cm^3

Hawaian low-density basalt
50% relative humidity

Freq. (Hz)	10^7	$3x10^8$	10^9	$3x10^9$
ε′	4.9	3.74	3.51	3.30
tan δ	.068	.085	.0481	.053
μ'/μ_o	1.047	1.047	1.040	1.035
tan δ_m	<.002	.0040	.002	.002

Figure 5.11
The effect of bound water in this sample of Hawaiian basalt is clearly shown; from (54). Very few data are available on this point for natural solids at microwave frequencies.

ues in one case, $CaCl_2$, are shown in Figure 5.12 from [85]. It is believed that all chloride pastes behave in a similar fashion but neither concentration nor mixture condition have been studied adequately according to Jain [72].

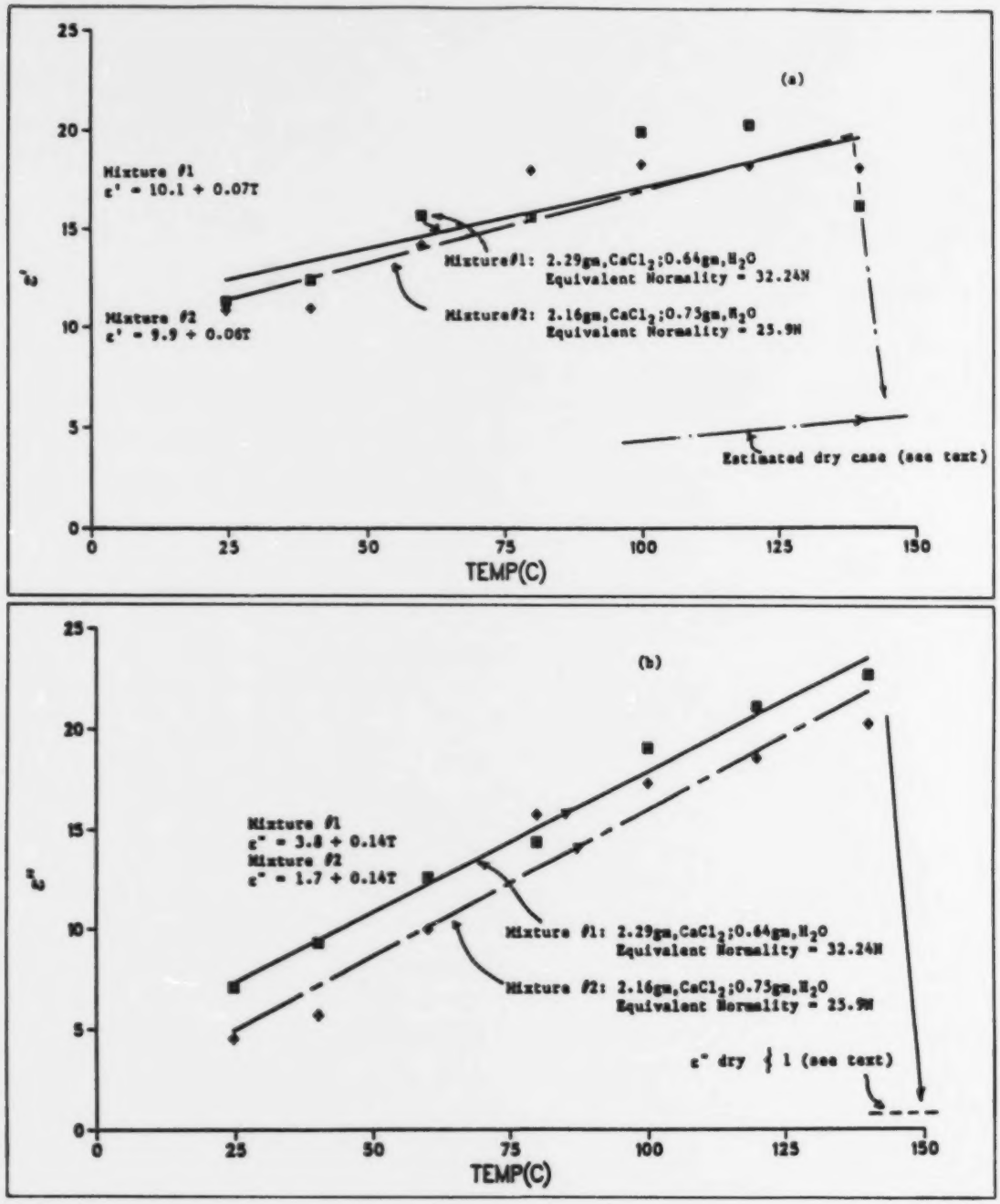


Figure 5.12
Dielectric data for two (typical susceptor) pastes of $CaCl_2$ in distilled water at 2.9 GHz. The arrows indicate the direction of temperature change in the thermostatically-controlled oven. Extreme-right-hand arrows show the observed trend for T>140°C. Dry powder values are shown (a) ε' (T), (b) ε" (T) (85).

6. High Temperature Dielectric Measurement Techniques

MANY SYSTEMS HAVE BEEN USED FOR MICROWAVE PROperty measurements of solid dielectric (ceramic and mineral) samples up to 2000°C. Chen's method is practical and repeatable by simply matching the microwave power required to the sample in a waveguide [18]. Their difficulty, and to an extent the difficulty with every method, is temperature measurement. A more elaborate method (and probably the best so far), which has been quoted by many writers, is due to Couderc et al [86]. A resonant cavity was used which heats in one resonant mode and allows the recording of the dielectric properties instantaneously through an adjacent frequency (low power) source through a different excitation mode, illustrated in Figure 6.1. They measured a few materials, including FeS; their T_E value agrees with that of Wong [46].

Wong's method [46] is a variation of Couderc's [86] with the advantage that the surface reflection coefficient can also be recorded; in other respects Wong's method is less precise and more cumbersome. However, it was the first versatile system made, and evolved from a ten year interest in the subject of dielectric mixtures at the University of Alberta. The method proposed for Part Two of this study is an adaptation of the one due to Couderc [86], using the precision handware design of Johnson and Brodwin [87] in the sintering of ceramics—SiC and $A1_2O_3$. This study [87] is notable for its attention to cavity design methods, in particular high temperature movable cavity end-walls (short circuits).

For *in-situ* measurements, the method described by Ulaby [19] has the greatest potential. Theory and method are described (with computer programmes for solving the equations) by hp [75] in great detail for confined samples—and can be related directly to *in-situ* methods using the measurement applicators described and referenced by Ulaby [19]. The technique is not restricted to one temperature; in fact, it is a suitable method for recording rapid changes in properties in "free space" in general, but it does require one prepared surface on a sample (or rock face) and careful attention to thickness: either "infinite" or known exactly.

Laboratory test cells have been described by a number of other writers, including Webb and Church [88]. Temperature measurement and control remain the major problems in relating chemical and structure changes to ε', ε'', dT/dt and the incident power density. Elaborate techniques have been used for studying dT/dt effects with graphite (interactive) heating elements on a ceramic sample in a cavity, but the results, reported only briefly, are difficult to interpret [89]. The method used by Atomic Energy of Canada Ltd., Chalk River Nuclear Laboratories for this project is described in the following section [91].

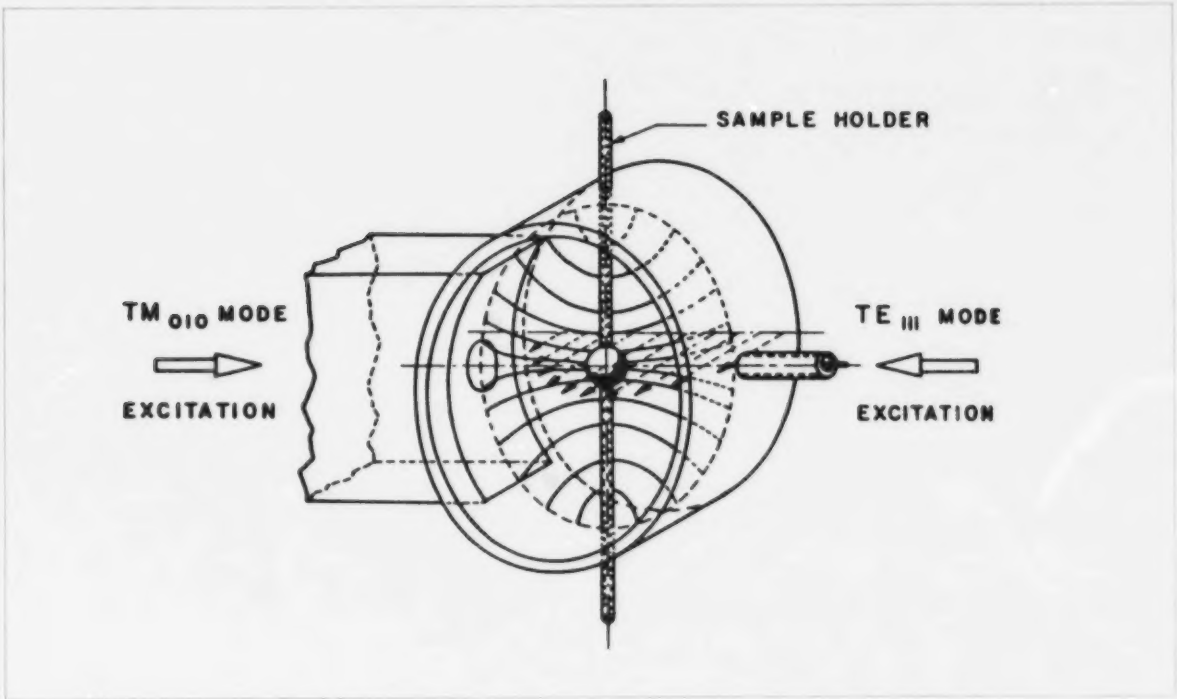


Figure 6.1
A microwave heat and measure system due to Couderc, Giroux and Bosisio (86). The test sample is heated in the TM_{010} mode-broken field lines—and the perturbation of the TE_{111} mode at low power excitation used to measure the dielectric data in terms of the shift of that mode's resonant frequency (ε') and change of Q (bandwidth—ε'').

Part Two: TESTS OF ONTARIO'S INDUSTRIAL MINERALS

By: F.C. Iglesias, C.E.L. Hunt, R.M. Hutcheon, G.W. Wood, R.D. Barrand
Atomic Energy of Canada Limited Research Company

7. Introduction

THE GENERAL AREA OF STUDY OF MICROWAVE INTERACTIONS with matter has been of increasing interest to Chalk River over the past few years. The potential advantages of microwaves as an energy delivery agent have been tested in applications ranging from the melting of nuclear fuel, the plasma discharge, and dissociation of process gases, to the treatment of psoriasis with microwave induced hyperthermia. As yet, no conclusive evidence has been found for non-thermal effects of microwaves (except in gases), although there are suggestions of such effects in biological systems. Also, the increased rate of rock sample dissolution induced by a microwave field has not been quantitatively understood.

The present study called for the testing of eight samples, four obligatory materials and four selected on the basis of the literature search covered in Part One of this report.

The obligatory materials were:

talc
talc with binder
nepheline syenite
kaolin

Tests were recommended on the following options:

serpentine minerals
illite-montmorillonite clay, shale
vermiculite
magnetite.

Analyses of samples before and after microwave treatment, are considered essential. A small change in bound water content, for example, may change the microwave loss factor by one order of magnitude at elevated temperatures. A 1-10% content change in certain metal oxide impurities at critical geometries is predicted to have a similar effect.

In all cases, impurities (associated microwave active minerals) and bound water are considered critically important to microwave heating.

Materials were supplied by the Mineral Development Section, Mineral Development and Lands Branch of the Ontario Ministry of Northern Development and Mines. These were:

1. Serpentine—a crushed sample with some magnetic separation, Hedman Resource Ltd., Warden and Munro Townships, Northern Ontario.
2. Nepheline Syenite—dry ground with electromagnetic separation, "340" product from Indusmin Division of Falconbridge Ltd., Nephton, Ontario.
3. Illite clay—air dried, Canada Brick quarry, Dundas, Ontario (Arkona Formation).
4. Kaolin-crude ore sample with silica, air dried, from Kipling Township, Northern Ontario.
5. Vermiculite, from Cargill Township, Northern Ontario.
6. Magnetite concentrate, by-product concentrate from Indusmin Division of Falconbridge Ltd., Nephton, Ontario.
7. Talc—ground with electromagnetic separation, "FDC" grade product from Luzenac Inc., Timmins, Ontario.

For the eighth sample, a sodium silicate binder, labelled "product E" (containing sodium silicate), was supplied from National Silicates Ltd., Toronto, Ontario with the request that it be combined with talc to provide the additional test sample. A sample of 5% binder (product E), 95% talc, was prepared and tested as sample #8.

Chemical analyses were supplied with most of the samples and are included with the experimental results.

8. Test Procedures

General

The purpose of the experiment was to measure the dielectric properties of the selected minerals as a function of temperature up to about 800°C. In order to interpret the dielectric measurements some auxiliary experiments were required. First, the as-received material was characterized using metallographic techniques and the particle size distributions were measured. Second, samples were heated to 800°C and re-examined to determine any effect of temperature on the mineral structure. Third, samples were irradiated in a 1.4 kW microwave oven for up to 20 minutes to indicate gross interactions with a microwave field and to indicate any physical or chemical changes.

Preliminary Tests

Samples of about 20 g were heated for 15 minutes at 800°C in a standard laboratory tube furnace. Samples of as-received and heated material were mounted in epoxy, rough polished and examined with a metallurgical microscope at magnifications up to 400 times. Photomicrographs of the as-received and heated samples are shown in the sections describing the results of the individual minerals. Observations of any change were made by microscope in reflected light only and may therefore have been limited in detection. Only serpentine and magnetite showed no change to the naked eye but both showed some change under magnification. Some of the materials which showed visible changes, e.g. colour, showed little difference under magnification. Vermiculite, as expected, expanded significantly but showed no other changes, either in colour or under microscopic examination. Because of these apparent changes, it was decided to test microwave measurements at a series of ascending temperatures, in addition to the procedure of heating the sample to the maximum temperature and measuring the microwave properties continuously while cooling. A final room temperature measurement was made to judge the effects of any permanent changes produced by heating.

Approximately equal volumes of each of the samples supplied were sieved to obtain an indication of the particle size distribution. Sieves were manufactured by Endecotts Ltd., London, England to ASTM standards.

Initial tests were designed to establish the overall behaviour of each material in a microwave field. A sample, typically about 10 g, was loaded into a microwave cavity and monitored by a thermocouple grounded to the cavity. Samples were heated either in air or in flowing argon at input power levels of 0.5, 1.0 and 1.5 kW. This technique was unsatisfactory because at a power of about 1 kW arcing occurred between the thermocouple tip and the material, resulting in erroneous readings. To overcome this problem, samples were then placed in a 1.4 kW microwave oven, heated for two minutes and the temperature measured as soon as the microwave power was shut off. Other samples of most materials were then heated in the same man-

ner for 20 minutes. These samples were then sieved and compared with the as-received measurements.

The only materials which showed significant reaction in the 1.4 kW oven were magnetite and vermiculite. These were retested in the high-power unit without any temperature measurement, the magnetite at about 2 kW with flowing argon-2% hydrogen, to see if any reduction occurred and the vermiculite at 5 kW, to maximize the power input.

Microwave Measurements

General

All tests were done at 2385 MHz. The purpose was to measure the complex dielectric constant, ε^*_r (where $\varepsilon^*_r = \varepsilon'_r - i\varepsilon''_r$ and $i = \sqrt{-1}$), as a function of temperature. Both the real part, ε'_r, and the absorptive part, ε''_r, of the dielectric constant are usually temperature dependent.

Any processing of a mineral using microwaves will depend on whether microwaves are absorbed, transmitted or reflected. Possible industrial uses of minerals in a microwave field will depend on the same properties. Frequently, the microwave behaviour of a material can be dominated by the properties of some impurity. Absorption of microwaves will result in conversion of the energy to heat. This may result in an increased rate of a chemical reaction or thermal stresses may be generated which can cause fracture of the material. Such reactions could assist further processes, e.g. milling, fabrication, chemical or biological leaching.

Temperature caused changes in most of the samples, even if it only drove off absorbed water. The decision was therefore made to measure the dielectric constants while heating the samples to successively higher temperatures. Measurements were also taken at room temperature on samples which had been previously heated to 800°C and for a few materials, measurements were made while cooling a sample from 800°C.

Dielectric Constant Measurement

The dielectric constant consists of two components, a real and an imaginary part. The real part of the dielectric constant, ε', varies little with temperature for any of the materials tested. Except for vermiculite, all changes in ε' over the temperature range 20° to 800°C were 30% or less. Values for ε'', the imaginary (or absorptive) component, varied widely, often by an order of magnitude. This component is the one most indicative of the microwave power absorbed by the sample.

The measurement technique, based on the Slater perturbation theorem, measures the change in frequency, Δf, and the change in quality factor, ΔQ, of a resonant cavity when a precise volume, Δv, of the candidate material is introduced. It may be shown that:

$$\frac{\Delta f(T)_{resonance}}{f_{resonance}} \approx \frac{k_1 v_s [\epsilon'_r(T) - 1]}{[1 + (\epsilon'_r(T) - 1)k_2]}$$

and

$$\Delta\left(\frac{1}{2Q}\right) \approx \frac{k_1 v_s \epsilon''_r(T)}{[1 + (\epsilon'_r(T) - 1)k_2]}$$

where
- f = resonant frequency
- k_1, k_2 = constant, depending on sample shape and electric field distribution
- v_s = sample volume
- Q = cavity quality factor
- T = temperature

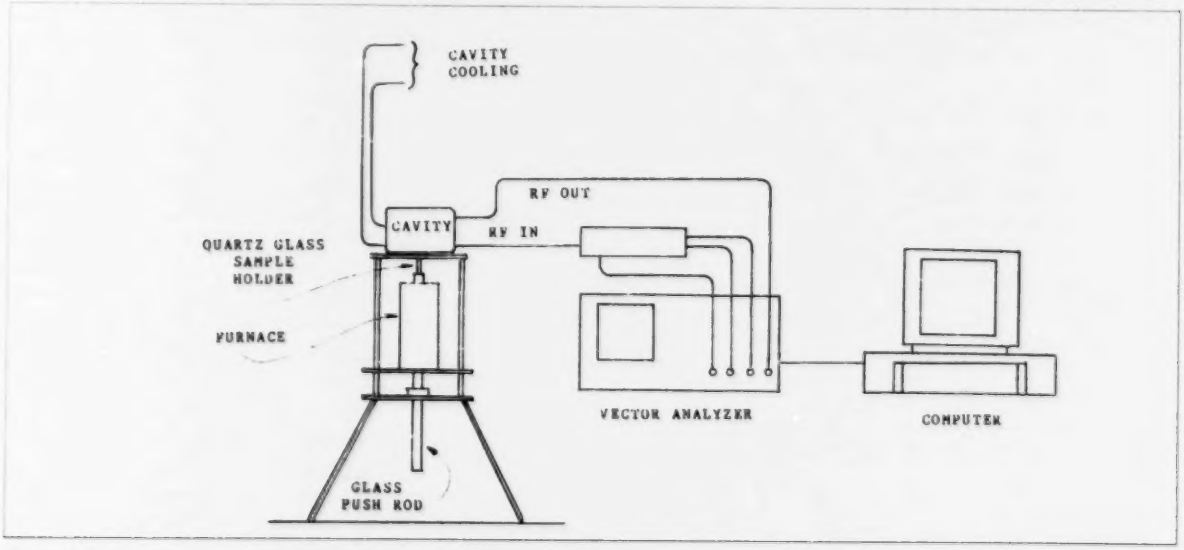


Figure 8.1
Schematic of test arrangment for measurement of dielectric constants.

These equations only yield relative values of ε' and ε'' as a function of temperature. Absolute values may be deduced by comparing the relative values of the candidate materials with values obtained from "standard" materials for which accurate values are available.

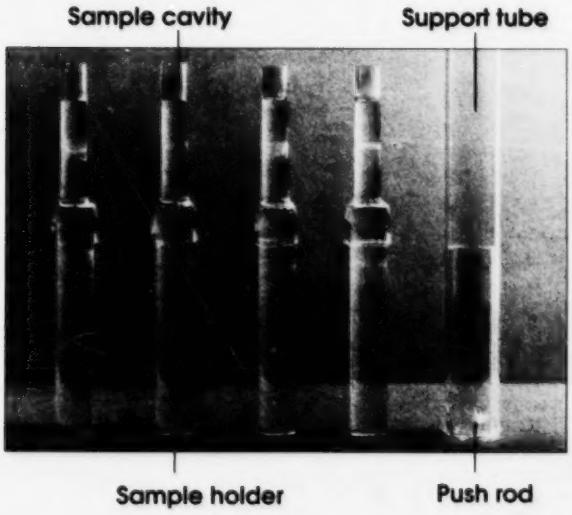


Figure 8.2
Sample holders and push rod.

The present system (Figures 8.1 to 8.4) consists of a TM_{010}-like cavity with a sample and sample holder inserted into it, the holder being a hollow quartz tube. The frequency and quality factor (Q) of the cavity are measured by an HP Network Analyzer which is controlled by an IBM-XT PC using the GPIB interface protocol. The frequency and Q are measured every 0.6 seconds and then recorded in a data file for later corrections and calculations. The sample can be heated up to 1000°C in a small resistance furnace which is mounted directly below the water cooled cavity. After heating to the selected furnace temperature, the sample is rapidly (≈ 1 s) inserted into the cavity and the computer starts the measurement sequence and records the elapsed time, frequency and Q. The time may later be used with a calibrated cooling curve function to give the temperature.

The present apparatus can measure either the electric or magnetic properties of materials at 2.45 GHz, depending upon the location of the material sample in the TM_{010}-like cavity. In electric mode, the system simultaneously measures the real and absorptive parts of the relative permittivity (ε'_r and ε''_r respectively); in magnetic mode it measures the real and absorptive part of the relative permeability (μ'_r and μ''_r). In fact, the calibrated system measures values which are *normalized* to the free space values ε_o and μ_o—in other words, the values in this report are relative values. For example, ε''_r is

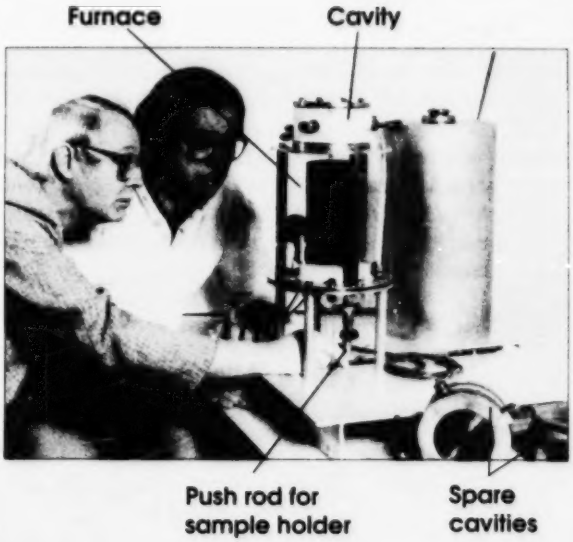


Figure 8.3
Experimental arrangement for dielectric measurements.

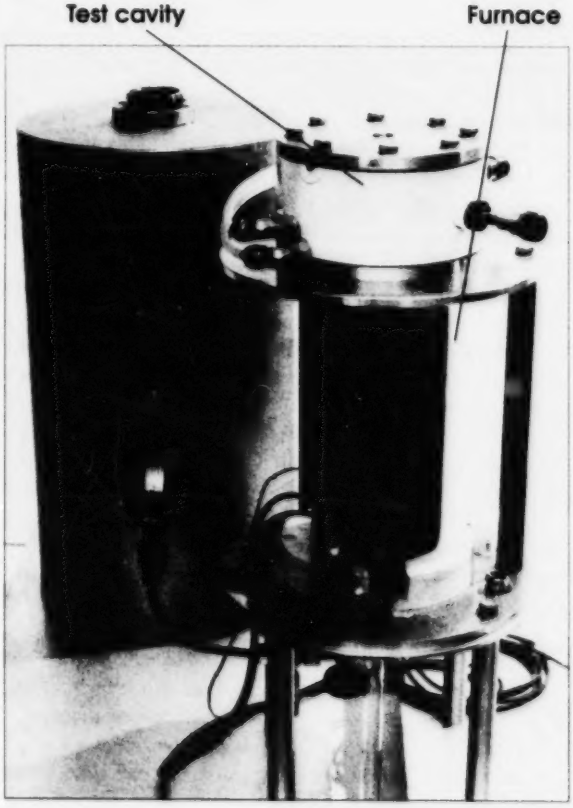


Figure 8.4
Detail of test cavity and furnace.

actually $\varepsilon''_r/\epsilon_0$). Throughout the rest of this report, the subscript will be dropped.

Measurements were made using samples of about 0.1 ml. Samples were heated to test temperature in a cylindrical furnace located immediately below the test cavity (see Figures 8.1 to 8.4). When the sample reached the test temperature, it was raised into the cavity and readings of the frequency shift and quality change were immediately taken. The sample was then lowered back into the furnace and heated to the next test temperature.

High-Power Tests

Several high-power tests were tried under controlled (inert or oxidizing) atmosphere. About 10 g of sample was loaded into a boat in a glass tube which passed through the microwave cavity. The glass tube was used to permit a controlled gas atmosphere surrounding the sample. A thermocouple grounded to the microwave cavity was used to monitor the sample temperature. The gas atmospheres used were argon and air.

The results were disappointing. At input power levels between 1 and 1-1/2 kW, arcing started, apparently initiated at the thermocouple tip in spite of it being grounded to the cavity. Arcing started at a lower power in an argon atmosphere than in air. Optical pyrometer temperature measurements were not possible without considerable modification of the test arrangement and cavity. This type of testing was therefore abandoned for the present test series since the fundamental ε^* measurements were considered to be of greater value. Instead some tests, without continuous temperature measurement, were done in a commercial microwave oven.

Samples, again of about 10 g, were placed in a commercial microwave oven with a rated microwave power of 1.4 kW. Each sample was irradiated for two minutes and the temperature measured by inserting a thermocouple immediately after the power was cut off. Except for the magnetite, which reached 728°C, and the vermiculite which expanded in the normal fashion, there was only minimal response to this treatment.

9. Experiments On Selected Industrial Minerals

9.1 General

Of the eight samples tested, only the nepheline syenite and the magnetite had the appearance of a completely dry, free flowing sand. All the other samples were suspected of containing some moisture and contained some bound water (in the form of hydroxyl ions) which, according to the phase diagrams, may be driven off by heating up to 800°C. Examination of the ε'' results confirms that illite, kaolin and vermiculite contained unbound water which was quickly driven off. All three show a dramatic drop in ε'' between 110° and 200°C. The repeat room temperature measurement looks reasonable if one were to extrapolate the higher temperature values back to room temperature. Talc shows no effect of unbound water and, after heating to 800°C, returned to almost the original value. This suggests that although conversion of talc to enstatite and silica with the loss of bound water is expected, little chemical change in fact occurred. The talc plus binder, sample #8, dramatically shows the effect of unbound water contained within "product E". The initial value of ε'' is about 30 times that of talc without the binder, but, once the moisture was driven off, the curve closely followed that of pure talc.

Of those containing bound water, which should be driven off by heating to 800°C, only serpentine showed evidence of a continuous and permanent change in ε'', which continually decreased with increasing temperature. The repeat measurement at room temperature, after heating to 800°C, was close to the final value reached at 800°C, suggesting that the product material, with bound water driven off, has an ε'' which is not very temperature sensitive.

9.2 Serpentine

Summary

Serpentine, a product from Hedman Resources Limited, Warden and Munro Townships in Northern Ontario, was received in the form of a fine grained, light-grey powder. Microwaving in a 1.4 kW oven for 20 minutes produced little change and heated the sample to only about 290°C. However, this procedure did produce a marked change in the dielectric constant measured at room temperature. Not all of this change can be accounted for by driving off absorbed water.

Most of the minerals showed a change in the imaginary part of the dielectric constant, ε'' (which is the best indication of the microwave energy absorbed), between the as-received material and a sample which had been heated to 800°C and cooled. This change could usually be explained by evaporation of absorbed water. Serpentine, on the other hand, showed a continuous irreversible change with heating which cannot be explained in this way. At about 600°C serpentine is reported to decompose into forsterite, silica and water. The ε'' data suggests that this reaction may start at a lower temperature, possibly 400°C, and continue up to the highest temperature reached, 800°C. Since this is a solid state reaction it will

depend on both time and temperature. This may account for the unexpectedly large change in room temperature ε'' obtained from the sample heated in the microwave oven, in spite of the apparently low (290°C) temperature reached by this sample. The microwave radiation may also have affected the rate of reaction, since 290°C seems to be an excessively low temperature to drive off chemically bonded water. Alternatively, the temperature of the sample may have been higher, midway through the test, than at the end when the measurement was made. However, there was not the drastic colour change that was observed when a sample of the powder was heated to 800°C in a standard tube furnace.

Expected Behaviour

Weak binding forces between molecular chains where a fibrous structure occurs, iron protoxide replacement and nickel impurities, together with bound water, suggest the existence of several high frequency loss mechanisms. These may vary significantly from sample to sample.

Heating serpentine to temperatures above 600°C should produce irreversible chemical changes according to the equation:

$$2\,Mg_3(Si_2O_5)(OH)_4 \rightarrow 3\,Mg_2SiO_4 + SiO_2 + 4\,H_2O$$

[Serpentine → Olivine (Forsterite) + Silica + Water]

Thermal analysis curves show an endothermic reaction in the temperature range 700°- 800°C, corresponding to the release of structural water ($2\,(OH)^- \rightarrow H_2O + O^{-2}$), and an exothermic peak in the range 800°-820°C [92].

Experimental Results

Sample As-received

A sample of fine, white, powder labelled "Serpentine (product)" was supplied by the Ministry of Northern Development and Mines. A chemical analysis, provided by the Ministry, is given in Table 9.1.

Table 9.1
Chemical Analysis of Serpentine Sample

SERPENTINE	$Mg_3(Si_2O_5)(OH)_4$		
(product)	(Typical analyses of serpentine)	SiO_2	41.83%
		TiO_2	0.02
		Al_2O_3	0.30
		Fe_2O_3	1.29
		FeO	0.08
		MnO	0.04
		MgO	41.39
		CaO	tr
		H_2O+	13.66
		H_2O	1.57

Some of the powder was sized using a set of ASTM standard sieves manufactured by Endecotts Ltd., London, England. The measured weights retained in each sieve are listed in Table 9.2 and are shown graphically on Figure 9.1a.

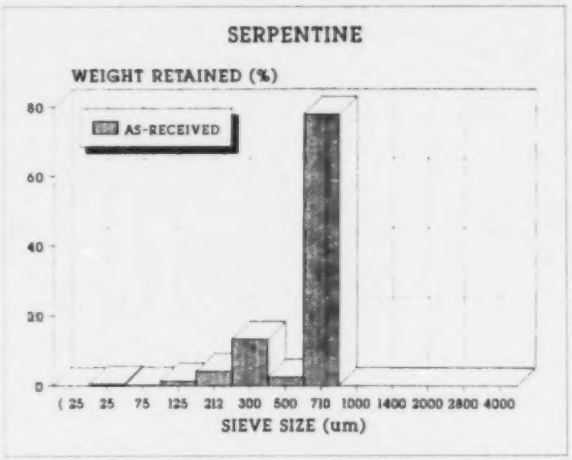


Figure 9.1a
Particle size distribution of as-received serpentine.

Table 9.2
Sieve Size Results for Serpentine Sample After Shaking for 0.5 h

	Sieve Size		% Weight Retained As-received	Microwaved
A	4.00	mm	0	0
B	2.80	mm	0	0
C	2.00	mm	0	0
D	1.40	mm	0	7.62
E	1.00	mm	0	0.16
F	710	µm	77.86	39.36
G	500	µm	2.44	31.77
H	300	µm	13.20	17.57
I	212	µm	4.14	0.82
J	125	µm	1.30	1.52
K	75	µm	0.16	0.25
L	25	µm	0.44	0.70
	<25	µm	0.02	0.24

Microwave Treated Material

About 35 g of powder was heated in a 1.4 kW microwave oven for 2 minutes and for 20 minutes. Heating for 2 minutes raised the bulk temperature of the powder to 130°C and 20 minutes raised it to 288°C. The powder was again sieved and the results are shown on Table 9.2 and Figure 9.1b.

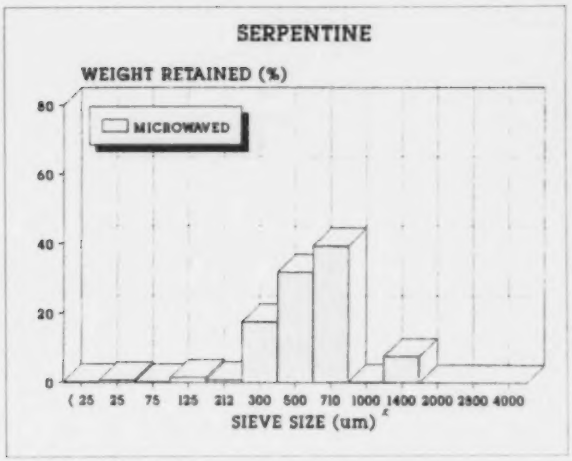


Figure 9.1b
Particle size distribution of microwaved serpentine.

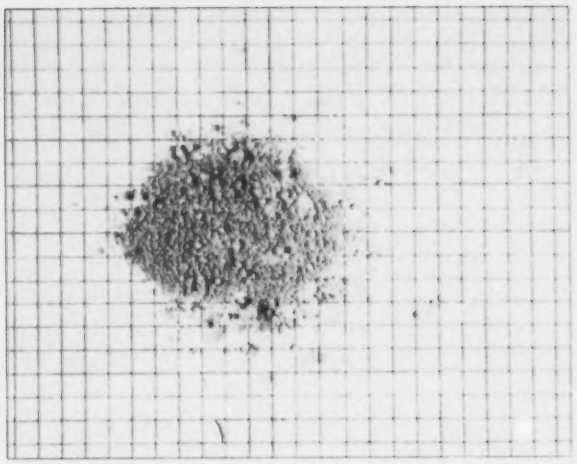


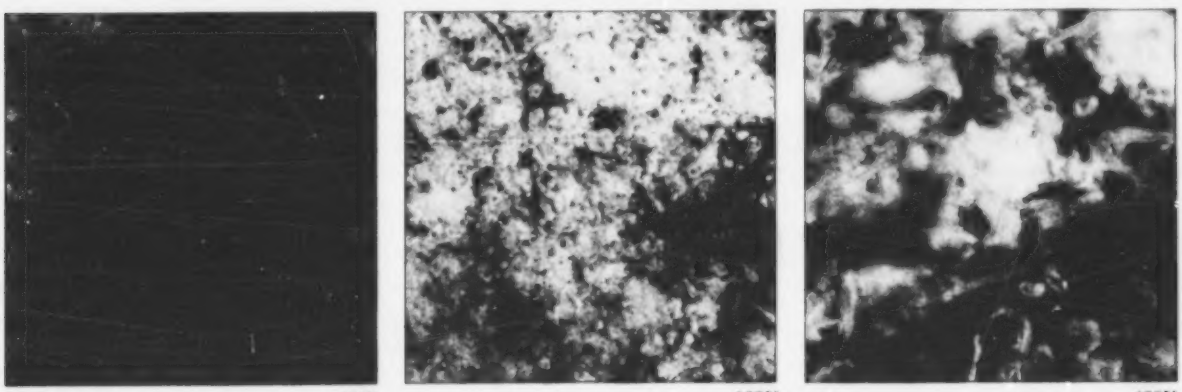
Figure 9.2
Serpentine, as supplied.

The as-received material was a loose, light-grey powder with a slight tendency to agglomerate into balls, probably due to absorbed moisture. The microwaved material had a slightly darker colour but appeared otherwise unchanged. The change in particle size distribution between the microwaved and the as-received sample may easily be explained by assuming that the 20 minute microwave treatment drove off all absorbed water.

Microscopic Examination

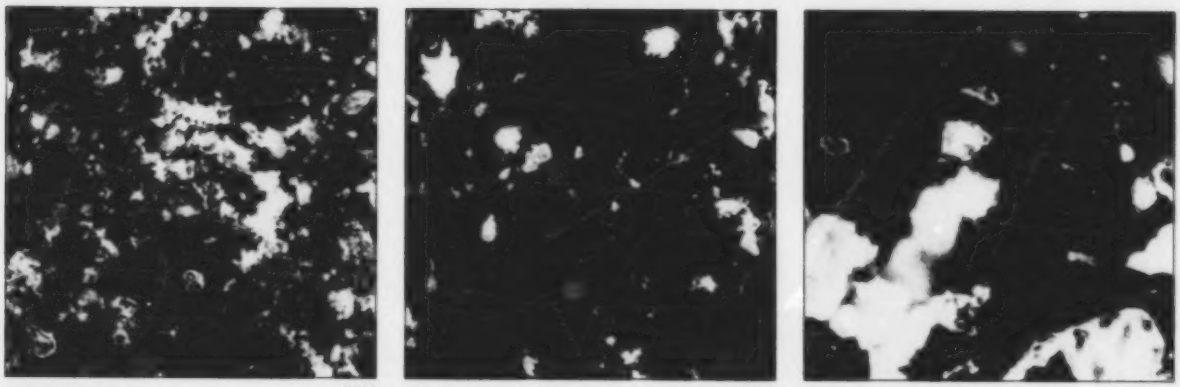
Microscopic examination was made of both as-received powder and a sample which had been heated in a laboratory furnace to 800°C for 15 minutes. 800°C was chosen as the maximum temperature for the dielectric constant measurements described in the next section. This temperature should also produce irreversible chemical changes as described above. A colour change from white to a dark brown was observed.

Figure 9.2 shows a macrograph of the as-received material. The lumps shown in the photograph disintegrated to a fine powder with a very light pressure. Microscopic examination showed little structure, partly because the particles were rounded and did not stick well to the mounting material. This made polishing without tearing out the particles difficult. Individual particles tended to be left as rounded surfaces, defying clear focusing, particularly at high magnification. Figure 9.3 shows the results. Slightly more success was obtained with the material which had been heated to 800°C (Figure 9.4), however, little change was visible microscopically. The only evidence of the expected chemical changes listed above was in the increased ease of preparing the metallographic samples and in the colour change.



50X 100X 400X

Figure 9.3.
Photomicrographs of as-received serpentine.



50X 100X 400X

Figure 9.4.
Photomicrographs of serpentine heated to 800°C for 15 minutes.

Dielectric Measurements

Measurements were done on several different samples at room temperature and at successively higher temperatures up to 800°C and during cooling from 800°C and on samples from previous tests (furnace heated to 800°C and microwaved for 20 minutes). The results are listed in Table 9.3.

Table 9.3
Dielectric Measurements for Serpentine, As-Measured and Normalized + to a Density of 1.25 g/mL

Temperature °C	Density g/mL	ε'		ε"	
		Measured	Normalized+	Measured	Normalized+
Room	1.23	2.42	2.44	0.073	0.074
	1.03	2.33	2.61	0.049	0.059
	1.25	2.61	2.61	0.074	0.074
	1.19	2.55	2.63	0.078	0.082
*	1.06	2.17	2.380	0.009	0.011
**	1.44	2.84	2.60	0.026	0.023
110	1.52	3.30	2.89	0.146	0.120
200	1.52	3.24	2.84	0.125	0.103
400	1.52	3.13	2.75	0.0969	0.080
600	1.52	3.32	2.91	0.0517	0.042
800	1.52	2.76	2.45	0.0122	0.010
Cooling curve					
700	1.01	2.13	2.40	0.0070	0.0087
600	1.01	2.06	2.31	0.0040	0.0050
500	1.01	2.02	2.26	0.0034	0.0042
400	1.01	1.97	2.20	0.0032	0.0040
300	1.01	1.93	2.15	0.0028	0.0035
200	1.01	1.91	2.13	0.0030	0.0037
100	1.01	1.88	2.09	0.0031	0.0038
50	1.01	1.76	1.94	0.0033	0.0041

+ Normalized is linear with density for (1- ε') and ε".

* Heated to 800°C cooled to room temperature and re-measured.

** Microwaved at 1.4 kW for 20 minutes.

Since different specimens were used, sample variation between tests resulted in variation in the measured dielectric constants. To compensate, all measurements were normalized to a nominal specimen density of 1.25 g/mL. This value was arbitrarily selected as being about the mid-range of the sample densities used. The normalized values of ε' and ε" are listed in Table 9.3 and plotted on Figures 9.4 and 9.6.

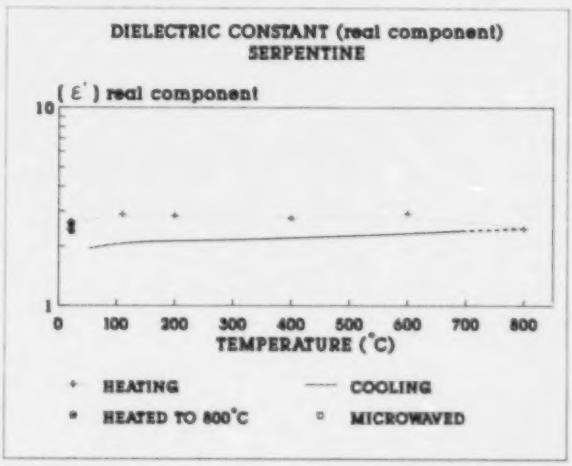


Figure 9.5
Real component of dielectric constant for serpentine during heating to, and cooling from 800°C.

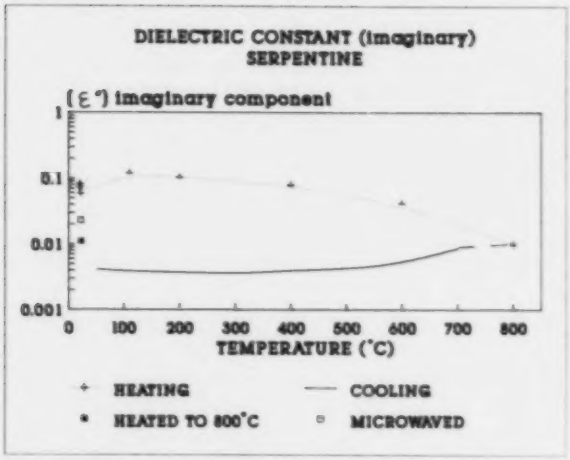


Figure 9.6
Imaginary component of dielectric constant for serpentine during heating to, and cooling from 800°C.

The real portion of the dielectric constant, ε', is not highly temperature dependent. The cooling curve is about 50% lower than the heating curve, suggesting that the heating cycle has resulted in physical and/or chemical changes. The imaginary portion of the dielectric constant, ε", shows this more clearly. During heating, there is a small increase to about 100°C, probably caused by absorbed water. From 100°C to 800°C, ε" continuously decreases, by an order of magnitude. The cooling curve, from 800°C to 50°C, shows a further decrease in ε" as the temperature decreases, the opposite behaviour to the heating curve. This strongly argues that the material being cooled is different from the material that was heated.

Two anomalies are shown: the sample that was heated to 800°C and retested at room temperature and the sample that was heated in the microwave oven. The sample heated to 800°C appears to be high when compared with the cooling curve. A probable reason is absorption of atmospheric moisture by the sample during storage. The heat-treatment and the dielectric constant measurement were several days apart. The more interesting anomaly is the sample which had been heated by microwaves. The peak recorded temperature was 288°C, much too low to produce the chemical changes predicted above. Consider how a sample could reach this end point by thermal means alone. During heating, ε" would follow the heating curve shown on Figure 9.6. During cooling it would probably follow a path parallel to the cooling curve. If this is correct, then to reach a room temperature ε" of 0.023, the heating cycle would have had to reach about 600°C. This suggests that the predicted chemical change is time as well as temperature dependent. It further suggests that a high frequency microwave field can increase the reaction rate, possibly by several orders of magnitude, since it has apparently occurred at a temperature 300°C lower than normally required.

Conclusions

The "serpentine product" tested in this work interacted only moderately with 2.450 GHz microwaves. A sample irradiated in a 1.4 kW microwave oven for 20 minutes was measured at 288°C at the end of this time.

Both the real and imaginary portions of the dielectric constant were measured during heating and cooling over the temperature range from room temperature to 800°C. Heating to 800°C seems to produce physical/chemical changes such that the dielectric constant on cooling showed completely different characteristics to that on heating.

Heating serpentine in a microwave oven produced no visible physical changes (e.g. particle size), but measurements of the dielectric constant suggest that chemical changes, which normally occur at much higher temperatures, may have occurred. If this behaviour is confirmed, then microwave fields may successfully substitute for high-temperature furnace treatments.

Recommendations

Serpentine which has been heated to 800°C has a low dielectric constant and hence is a low loss material. As such, it may be of interest for fabricating components for microwave circuits. This would require similar measurements on massive or sintered material rather than the powder used here.

Massive serpentine is soft and therefore easily shaped. Forsterite, on the other hand, has a hardness in the range of 6 1/2 to 7. At present, fabrication of ceramic parts made of forsterite would require heating of the pre-machined serpentine to ~800°C. The likelihood of damage from thermal stresses or steam generation is large. However, if microwaves can accomplish the same chemical conversion at a much lower temperature, such stresses may not be a problem. Further investigation should try to confirm that microwaves do promote chemical change at low temperatures and then investigate the consequences of producing the chemical change in massive material as well as in powder.

9.3 Nepheline Syenite

Summary

Nepheline syenite, a "340" product from the Indusmin Division of Falconbridge Ltd., in Nephton, Ontario, was received as a fine grain free-flowing powder. Microwaving at 1.4 kW for 20 minutes raised the temperature to about 130°C and produced no visible changes. Heating a sample to 800°C for 10 minutes in a standard laboratory furnace also produced no visible changes.

The imaginary portion of the dielectric constant, ε", which is a good measure of the amount of microwave energy absorbed, showed a regular increase with increasing temperature. There was some difference between the values of ε" measured during heating and those measured during cooling, on two separate samples, but this may just be an indication of the

scatter in data to be expected with measurements of small values.

Because of the relatively simple phase diagram of nepheline syenite, with no chemical changes caused by heating, a sample was melted at 1460°C in an alumina crucible. The density increased by about 30% over that of loose powder, but numerous included bubbles kept the density well below theoretical. In an approximate way, a 30% increase in density would be expected to produce a similar increase in ε", while in fact the measured increase in ε" was over 30 times. X-ray analysis showed that, after melting and cooling to room temperature, the material was amorphous. This result suggests either that the mechanisms involved in absorbing microwave energy are different in a crystalline and an amorphous material, or that the bubbles in the solidified material are producing a Maxwell-Wagner effect at microwave frequencies—the latter being highly unlike. Is this true of other materials, with either similar or different crystal structure? Does this provide a method of tailoring microwave absorption? Is it possible to develop a product transparent to visible light but opaque to microwaves? More studies like the present one are needed to answer these questions.

Expected Behaviour

Nepheline syenite is expected to be a medium to low loss material. The losses will probably be determined by impurities, e.g. biotite. Heating of nepheline is not expected to produce any irreversible chemical or physical changes [92]. It is stable over a wide range of sodium/potassium ratios. However, at low temperatures there is a miscibility gap between compositions in the range $NaKAl_4Si_4O_{16}$ and $KAlSiO_4$. The material used for these tests has a composition just within this miscibility gap and should therefore be a two-phase mixture. Heating to about 600°C should convert the structure to single phase. Thus heating to 800°C, as in these tests, should produce a physical change which theoretically would revert on cooling. However, the kinetics of both the forward and backward reaction may be slow at these temperatures. Solid state reactions involving covalent bonding can be slow at low temperatures.

Experimental Results

Sample as-received

A sample of white, free flowing, fine grained sand labelled "Nepheline syenite (product)" was supplied by the Ontario Ministry of Northen Development and Mines. A chemical analysis, provided by the Ministry, is given in Table 9.4.

Table 9.4
Chemical Analysis of Nepheline Syenite Sample

Nepheline Syenite (product)			
	Main mineralogy:	nepheline $Na_3(Na_1K)(Al_4Si_4)_{16}$ feldspar (K, Na) $(AlSi_3O_8)$	
	(Typical analyses)	Fe_2O_3	0.10
		Al_2O_3	23.8
		Na_2O	10.4
		K_2O	4.8
		CaO	0.4
		MgO	0.04
		L.O.I.	0.3
		SiO_2	60.5
		(by difference)	

Some of the nepheline syenite was sized using a set of ASTM standard sieves manufactured by Endecotts Ltd., London, England. The measured weight percentages retained in each sieve are listed in Table 9.5 and are shown graphically on Figure 9.7.

Table 9.5
Sieve Size Results for Nepheline Syenite Sample After Shaking for 0.5 h

			% Weight Retained	
	Sieve Size		As-received	Microwaved
A	4.00	mm	0	
B	2.80	mm	0	
C	2.00	mm	0	
D	1.40	mm	0	
E	1.00	mm	0	
F	710	µm	0	
G	500	µm	0.48	0.54
H	300	µm	34.14	31.95
I	212	µm	26.52	27.02
J	125	µm	27.60	28.32
K	75	µm	8.90	9.80
L	25	µm	2.28	2.23
	<25	µm	0.06	0.08

Microwave treated material

About 65 g of the as-received nepheline syenite was heated in a 1.4 kW microwave oven for 2 minutes and for 20 minutes. Heating for 2 minutes raised the bulk temperature to 59°C and 20 minutes raised it to 132°C. The material was again sieved and the results are shown on Table 9.5 and Figure 9.7. There was no visible change caused by this treatment and no change in particle size.

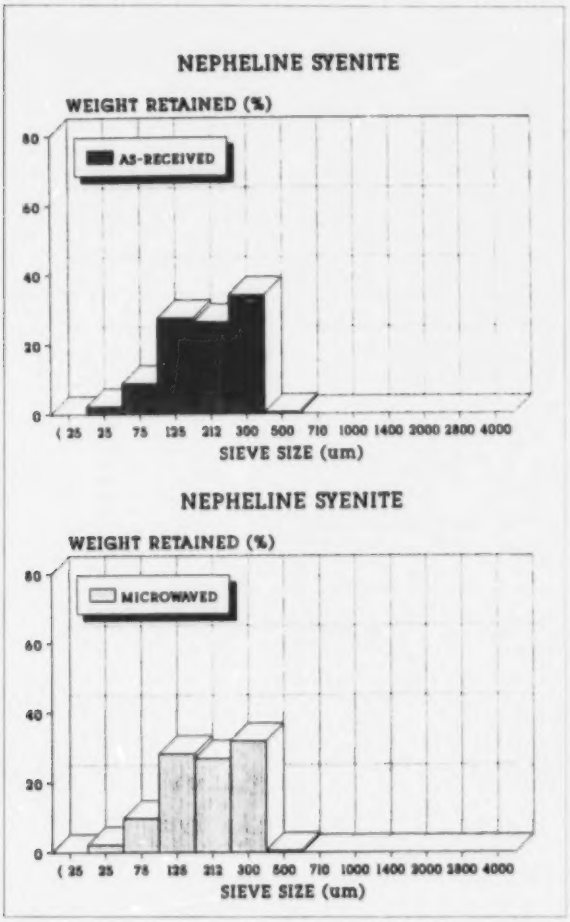


Figure 9.7
Particle size distribution of as-received and microwaved nepheline syenite.

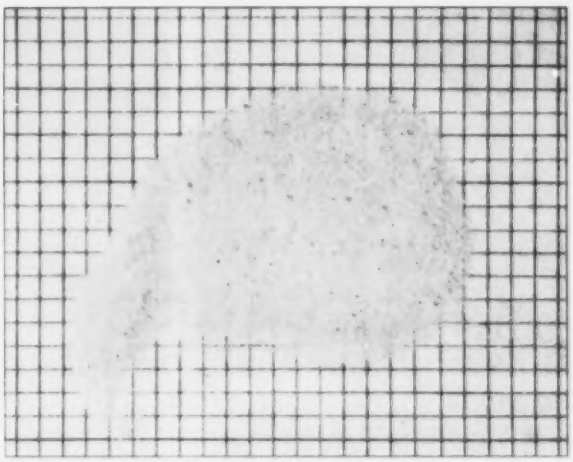
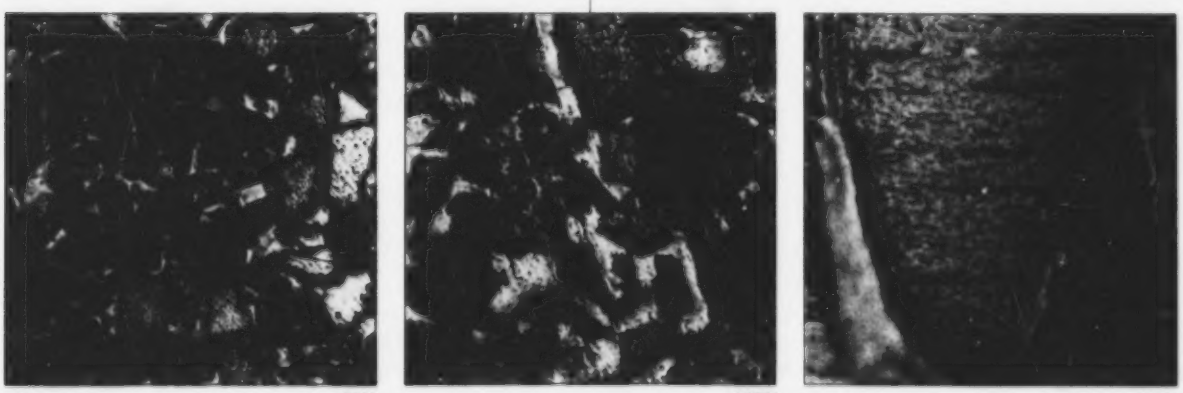


Figure 9.8
Nepheline Synite, as supplied.

Microscopic examination

A microscopic examination was done of both the as-received material and the material which had been heated in a laboratory furnace to 800°C for 15 minutes. 800°C was chosen as the maximum temperature for the dielectric measurements described in the next section. Figure 9.8 shows a macrograph of the as-received material. Figures 9.9 and 9.10 show micrographs of as-received and heated material respectively. The chemical analysis suggests that this material should lie within a two-phase region of the phase diagram. Heating above 600°C would bring it into a single phase region. The heating cycle to 800°C and back to room temperature should therefore have transformed the nepheline syenite first to a single phase material and then back to a two phase one. The photomicrographs show no apparent difference between the as- received and heated samples.



50X 100X 400X

Figure 9.9
Photomicrographs of as-received Nepheline Syenite.

50X

100X

400

Figure 9.10
Photomicrographs of nepheline syenite heated to 800°C for 15 minutes.

Dielectric Measurements

Measurements were done on several different samples at room temperature, at successively higher temperatures up to 800°C, during cooling from 800°C, on samples from previous tests (furnace heated to 800°C and microwaved for 20 minutes) and on melted material. The results are listed in Table 9.6.

Since different specimens were used, sample variation between tests resulted in variation in the measured dielectric constants. To compensate, all measurements were normalized to a nominal specimen density of 1.75 g/mL. This value was arbitrarily selected as being about the middle of the range of the sample densities used. Both ($\varepsilon' - i$) and ε'' vary linearly with density. The normalized values of ε' and ε'' are listed in Table 9.6 and plotted on Figures 9.11 and 9.12.

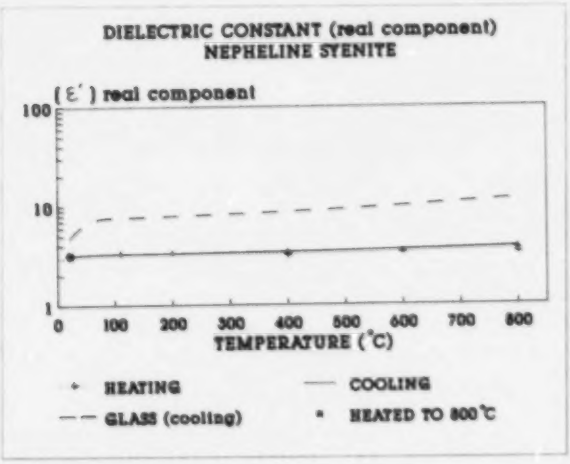


Figure 9.11
Real component of dielectric constant for nepheline syenite during heating to, and cooling from 800°C

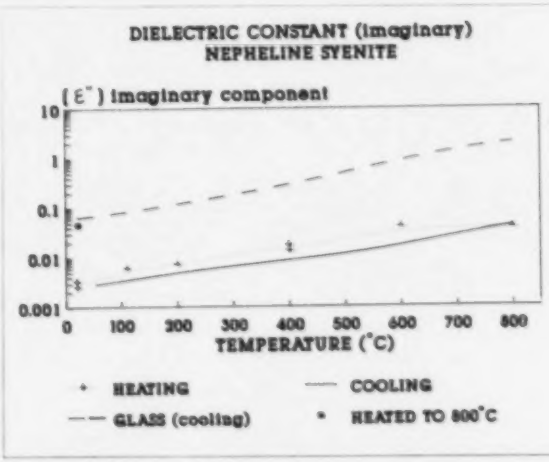


Figure 9.12
Imaginary component of dielectric constant for nepheline syenite during heating to, and coolin from 800°C.

Table 9.6
Dielectric Measurements for Nepheline Syenite, As-Measured and Normalized+ to a Density of 1.75 g/mL

Temperature °C	Density g/mL	ε'		ε"	
		Measured	Normalized+	Measured	Normalized+
Room	1.73	3.15	3.17	-	-
	1.81	3.23	3.16	-	-
	1.84	3.33	3.22	0.00356	0.0034
	1.58	2.96	3.17	0.0027	0.00226
	1.68*	3.12	3.21	0.00443	0.0046
	1.81*	3.24	3.16	0.00496	0.0048
	1.96**	5.16	4.71	0.0716	0.064
110	1.40	2.84	3.30	0.00495	0.0062
200	1.40	2.85	3.31	0.0059	0.0074
800	1.40	3.13	3.66	-	
400	1.81	3.29	3.21	0.0143	0.0138
600	1.81	3.43	3.35	0.0418	0.0404
800	1.81	3.42	3.34	0.0396	0.0383
Cooling curve					
800	1.43	3.30	3.81	0.0346	0.0423
700	1.43	3.20	3.69	0.0227	0.0278
600	1.43	3.12	3.59	0.0136	0.0166
500	1.43	3.04	3.50	0.0094	0.0115
400	1.43	2.99	3.44	0.0072	0.0088
300	1.43	2.95	3.39	0.0055	0.0067
200	1.43	2.88	3.30	0.0042	0.0051
100	1.43	2.88	3.30	0.0028	0.0034
50	1.43	2.86	3.28	0.0024	0.0029
Cooling Curve Glass**					
800	1.96	13.06	11.77	2.29	2.04
700	1.96	12.04	10.86	1.65	1.47
600	1.96	11.00	9.93	1.00	0.89
500	1.96	10.23	9.24	0.56	0.50
400	1.96	9.64	8.71	0.33	0.29
300	1.96	9.14	8.27	0.20	0.18
200	1.96	8.78	7.95	0.13	0.12
100	1.96	8.50	7.70	0.09	0.08
50	1.96	8.47	7.67	0.08	0.07

+ Normalized is linear with density for (1-ε') and ε"
* Heated to 800°C, cooled and measured at room temperature.
** Melted into a glass.

The real portion of the dielectric constant, ε', is only weakly temperature dependent over the temperature range from room temperature to 800°C. There is also little difference between the results measured during heating and during cooling. The imaginary (ε") portion, on the other hand increases an order of magnitude over the temperature range and there is a difference of up to a factor of two between heating and cooling curves. This may reflect transformation from the two-phase mixture suggested by the phase diagram to single phase during heating followed by possibly sluggish or incomplete separation during cooling, a not uncommon behaviour in solid state phase transformations.

Since the phase diagram indicated no chemical changes would be expected, a sample of the sand was melted in order to increase the density. About 20 grams were melted in a laboratory furnace at 1460°C, held for about 15 minutes and cooled to about 1000°C at a rate of 2°C/min. The resultant material contained many bubbles and, as a result, had only reached 80% of the theoretical density. The dielectric constant results were surprising. As shown on Figures 9.11 and 9.12, both ε' and ε" were strongly temperature dependent. The real portion of the dielectric constant, ε', was increased a factor of 5 over the as-received sand and ε" was increased a factor of 20. X-ray analysis showed that the melted material was a glass, further confirmation that the kinetics of phase transformation in this material are slow.

The loss mechanisms brought into play by transforming this material from a regular crystalline to an amorphous structure are not known, but further investigation of this and other materials with similarly sluggish phase transformation kinetics would be of interest. With such a large variation in dielectric constants between the two states, the possibility of tailoring materials for specifically required values may be feasible.

Conclusions

The nepheline syenite product tested in this work showed only weak interaction with microwaves. A sample irradiated for 20 minutes in a 1.4 kW microwave oven heated to about 130°C.

Both the real and imaginary components of the dielectric constant were successfully measured during heating and cooling over the temperature range from room temperature to 800°C. Heating and cooling produced different results, probably because of the sluggishness of the solid state phase transformation during cooling.

Melting of this nepheline syenite resulted in a porous glass which showed very much higher dielectric loss characteristics than the as-received crystalline material.

Recommendations

Nepheline syenite is a low-loss material at room temperature although the loss increases markedly with temperature. However, the most interesting aspect is the dramatic increase in dielectric constant in the amorphous state. Further work on the transformation kinetics from liquid to crystalline solid may lead to the possibility of tailoring materials for specific values of the dielectric constant.

In addition to studying the phase transformation kinetics, further work to establish the mechanisms of dielectric loss in the amorphous state compared with the crystalline state would be of use both for this and possibly for other materials.

9.4 Illite Clay

Summary

Illite samples were provided by Canada Brick Quarry, Dundas, Ontario (Arkona Formation). Illite clay is a dark grey material with a fairly even distribution of particle size ranging from coarse (1-2 cm) to fine (125 μm). Microwaving in a 1.4 kW microwave oven for 20 minutes, produced little visible structural change and heated the sample to about 260°C. Heating a sample to 800°C in a laboratory furnace changed the colour to dark brown but had little other noticeable effect.

Measurements of the imaginary part of the dielectric constant, ε", show a high microwave absorption at low temperature which drops by an order of magnitude by 150°C, presumably as a result of evaporating all the moisture. Samples heated either in the microwave oven or in the laboratory furnace and measured at room temperature, also had an ε" an order of magnitude lower than that of the as-received material.

Heating to 800°C should produce an irreversible chemical change by driving OH^- ions from the lattice (92). The ε" room temperature measurements on the heated sample suggest this reaction did not occur.

Expected Behaviour

Illite clay has both absorbed and bound water (in the form of OH^-) and therefore may be expected to show considerable reaction to microwaves. The chemical formula

$$K_{1-1.5}Al_4(Si_{7-6.5}Al_{1-1.5}O_{20})(OH)_4$$

shows considerable latitude in composition. The structure is layered. Water absorbed on surfaces and held between layers is easily driven off in the temperature range 100-200°C. In the temperature range 550°-650°C $(OH)^-$ ions are lost. Final disruption of the structure can be expected at temperatures over 850°C, higher than the test temperatures in this work. The driving off of $(OH)^-$ will represent an irreversible change leaving an unhydrated potassium aluminum silicate.

Experimental Results

Sample as-received

A medium grey sample varying from hard lumps to a fine powder, as shown on Figure 9.13, was supplied by the Ministry of Northern Development and Mines. The only chemical analysis provided was the formula listed above. Some of the material was sized using a set of ASTM standard sieves manufactured by Endecotts Ltd., London, England. The measured weight percentages retained in each sieve are listed in Table 9.13 and are shown graphically on Figure 9.14a.

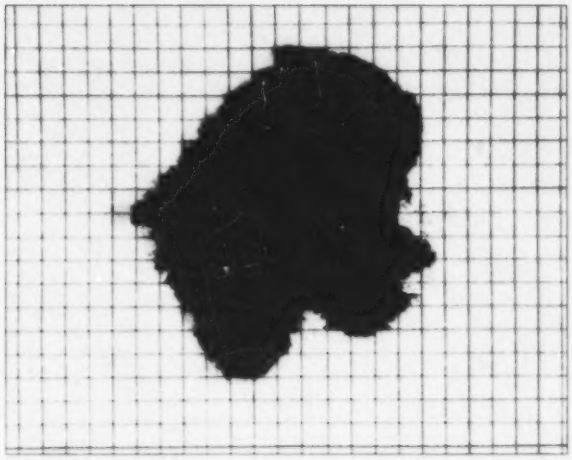


Figure 9.13
Illite clay, as supplied.

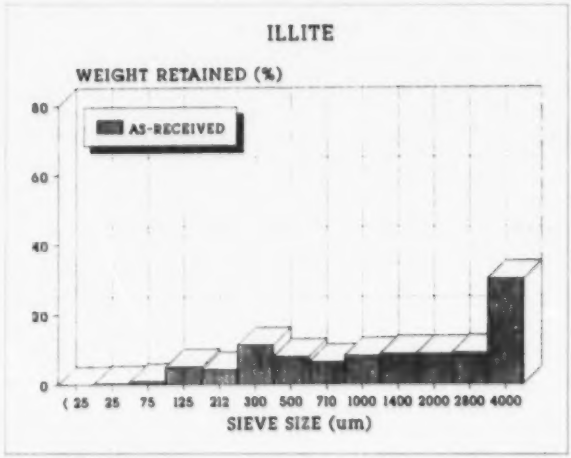


Figure 9.14a
Particle size distribution of as-received illite.

Table 9.7
Sieve Size Results for Illite Clay Sample After Shaking for 0.5 h

	Sieve Size		% Weight Retained As-received	Microwaved
A	4.00	mm	30.06	55.10
B	2.80	mm	8.96	5.67
C	2.00	mm	8.61	6.93
D	1.40	mm	8.65	6.62
E	1.00	mm	8.11	4.93
F	710	µm	6.34	4.22
G	500	µm	7.83	3.63
H	300	µm	11.16	4.09
I	212	µm	4.16	2.43
J	125	µm	4.98	2.97
K	75	µm	0.86	1.57
L	25	µm	0.26	1.55
	<25	µm	0.0	0.49

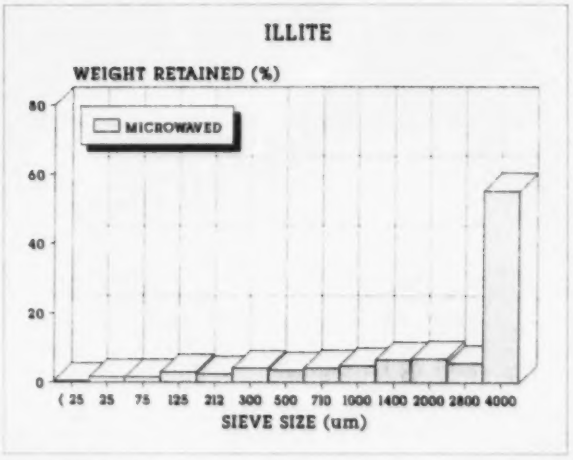


Figure 9.14b
Particle size distribution of microwaved illite.

Microwave treated material

About 75 g of illite clay was irradiated for 2 minutes and 20 minutes in a 1.4 kW microwave oven. Heating for 2 minutes raised the temperature to 165°C. Continued heating for 20 minutes raised it to 260°C. The material was again sieved and the results shown on Table 9.7 and Figure 9.14b. This treatment appeared to have driven off absorbed water but there was no other apparent change.

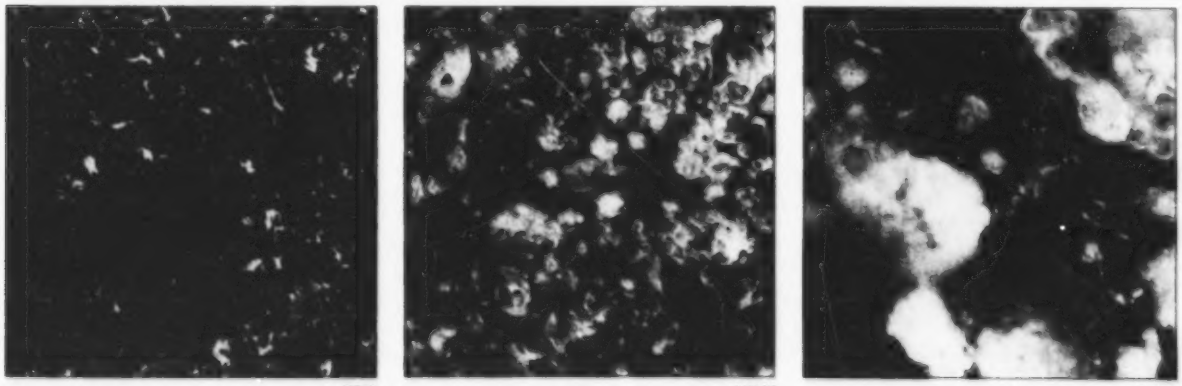
Microscopic examination

Microscopic examination was made of both as-received clay and some which had been heated in a laboratory furnace to 800°C for 15 minutes. 800°C was chosen as the maximum temperature for the dielectric constant measurements described in the next section. This temperature should also produce the predicted chemical changes described above. A colour change from grey to dark brown was observed.

Microscopic examination showed little structure, partly because sample preparation was very difficult. Particles did not stick well to the mounting material (epoxy) and tended to tear out during polishing. Figure 9.15 shows examples of the as-received material. The picture at a magnification of 100X shows typical examples of particle pull-out. At higher magnification (400X), particle rounding made focusing very difficult and structural features could not be seen clearly. The material which had been heated to 800°C, Figure 9.16, was much easier to handle. It is suggested that the moisture content of the as-received material was the cause of the preparation difficulties.

Dielectric Measurements

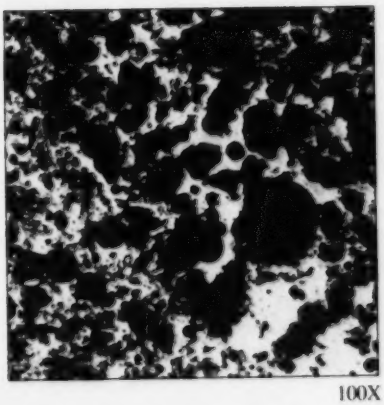
Since different specimens were used, sample variation between tests resulted in variation in the measured dielectric constants. To compensate, all measurements were normalized to a nominal specimen density of 1.8 g/mL. This value was arbitrarily selected as being about the mid-range of the sample densities used. Both (ε'-1) and ε'' vary linearly with density. The normalized values of ε' and ε'' are listed in Table 9.8 and plotted on Figures 9.17 and 9.18.



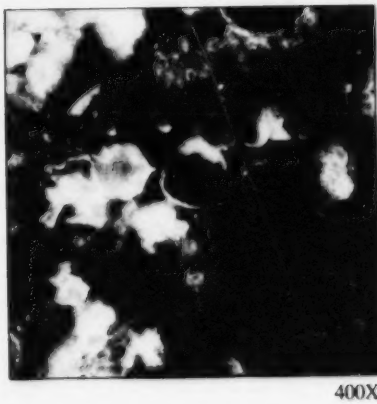
50X 100X 400X

Figure 9.15
Photomicrographs of as-received illite clay.

50X



100X



400X

Figure 9.16
Photomicrographs of illite clay heated to 800°C for 15 minutes.

Table 9.8
Dielectric Measurements for Illite clay, As-Measured and Normalized + to a Density of 1.8 g/mL

Temperature °C	Density g/mL	ε' Measured	ε' Normalized+	ε" Measured	ε" Normalized+
Room	1.80	4.80	4.80	0.714	0.714
	1.71	3.57	3.70	0.285	0.300
	1.58	3.58	4.08	0.436	0.497
	1.54	3.45	3.86	0.315	0.368
*	1.71	3.13	3.24	0.062	0.065
**	0.86	2.06	3.22	0.034	0.071
110	1.76	4.16	4.23	0.868	0.888
110	1.58	3.80	4.33	0.735	0.837
110	1.54	3.69	4.14	0.64	0.748
150	1.54	3.49	3.91	0.46	0.538
200	1.54	3.22	3.59	0.13	0.15
200	1.97	3.96	3.70	0.272	0.249
200	1.58	3.23	3.68	0.150	0.171
400	1.97	3.80	3.56	0.150	0.137
400	1.58	3.36	3.83	0.13	0.148
800	1.97	5.04	4.69	0.684	0.625
800	1.58	4.28	4.88	0.50	0.57
Cooling curve					
800	1.58	4.21	4.75	0.576	0.656
720		4.0	4.51	0.400	0.456
640		3.81	4.28	0.343	0.391
560		3.65	4.10	0.290	0.330
480		3.50	3.92	0.247	0.281
400		3.39	3.79	0.206	0.235
320		3.27	3.65	0.167	0.190
240		3.18	3.55	0.136	0.155
160		3.11	3.47	0.109	0.124
80		3.05	3.40	0.087	0.099

+ Normalized is linear with density for (1-ε') and ε".
* Heated to 800°C cooled to room temperature and re-measured.
** Microwaved at 1.4 kW for 20 minutes.

The real portion of the dielectric constant, Figure 9.17, shows the effect of absorbed water over the temperature range room temperature to 150°C. After this water was evaporated, the real component showed a weak temperature dependence over the remainder of the temperature range. The expected elimination of bound water in the form of $(OH)^-$ showed little effect. The imaginary portion of the dielectric constant shows a much more dramatic change in Figure 9.18. Evaporation of the absorbed water caused a sharp drop in ε". This drop continued up to 400°C. Heating from 400° to 800°C, the temperature range where elimination of the bound water $(OH)^-$ is expected resulted in a large increase in ε". The cooling curve did not retrace the heating curve, confirming that a chemical change had occurred in the material.

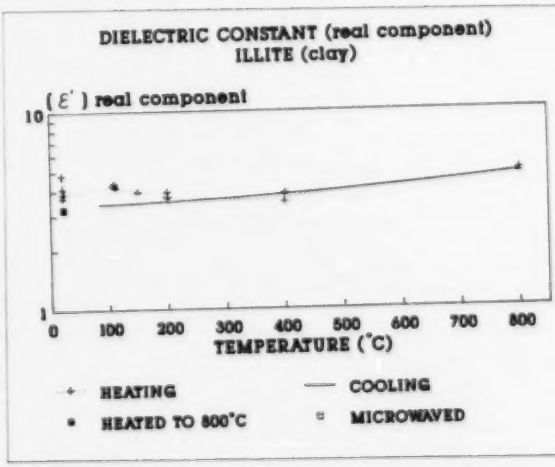


Figure 9.17
Real component of dielectric constant for illite clay during heating to, and cooling from 800°C.

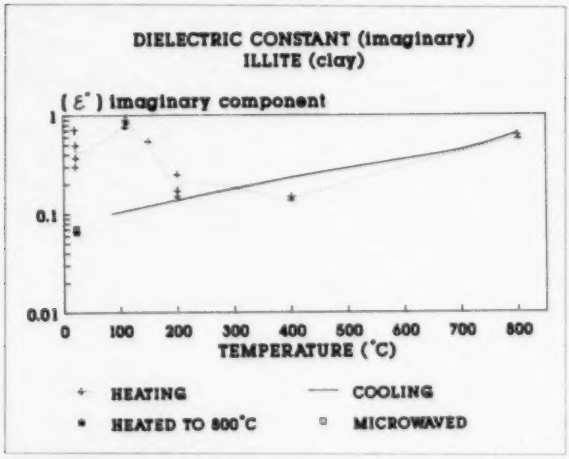


Figure 9.18
Imaginary component of dielectric constant for illite clay during heating to, and cooling from 800°C.

It is interesting to note that the room temperature measurements of both ε' and ε" for the sample heated to 800°C and the sample microwaved for 20 minutes (reaching a measured temperature of 260°C) are identical. The sample heated to 800°C had presumably released the bound water. This suggests either that the microwave irradiation also released the bound water, in spite of the low temperature measured or that at low temperature the bound water does not interact with the microwave field. Further work would be required to resolve this point.

Conclusions

Illite clay interacts only slightly with microwaves at room temperature. Irradiation for 20 minutes in a 1.4 kW microwave oven only raised the temperature to 260°C.

Both the real and imaginary components of the dielectric constant were measured during heating and cooling over the temperature range from room temperature to 800°C. Heating to 800°C caused chemical changes such that the dielectric constant during cooling was different from that during heating.

Heating illite in a microwave oven produced no visible physical changes but the dielectric constant measured at room temperature was the same as that measured on a sample which had been heated to 800°C.

Recommendations

Either bound water in the illite clay structure does not interact with microwaves at room temperature or low- temperature microwave irradiation has the same effect on driving off bound water as purely thermal treatments in the range 550° - 650°C. Further work should be done to establish which, if either, of these hypotheses is correct.

9.5 Kaolin

Summary

Kaolin was received from Kipling Township in northern Ontario, in the form of a white powder with a range of agglomerated particle sizes up to about 1 cm. The larger lumps were quite friable and could be crushed between one's fingers. Microwaving in a 1.4 kW oven for 20 minutes produced no measurable change.

The imaginary portion of the dielectric constant, ε", showed a rapid decrease between room temperature and 200°C. This decrease was probably caused by the drying of absorbed moisture. Over the temperature range 400°-525°C, water is expected to be released by the dissociation of OH^- ions from the lattice [92] leaving a mixture of Al_2O_3 and SiO_2. This may be indicated by the hysteresis between the curves obtained for ε" during heating and cooling. However, much of this apparent difference may represent experimental scatter at these low values, of the order of 0.005. These results suggest one of two possibilities: either the chemical change did not occur and the hysteresis is experimental scatter, or else the chemical change has only a small effect on ε".

Expected Behaviour

Kaolin is thought to be an extremely complex dielectric. The properties are known to vary greatly and there is a dielectric- properties relationship to zeolites. Microwave processing of kaolin, to remove pyrite impurities, has been reported in the literature.

The structure is layered, with structural OH^- ions. Loss of these ions, as water, usually occurs between 400° and 525°C [92]. There is variation between specimens, but all water derived from OH^- ions is expelled by 800°C.

Experimental Results

Sample as-received

The sample supplied by the Ministry of Northern Development and Mines was a white powder with some lumps which could be broken between the fingers. A chemical analysis, supplied by the MNDM, is given in Table 9.19.

Figure 9.19
Kaolin, as supplied.

Table 9.9
Chemical Analysis of Kaolin Sample

Kaolin
W. Silica
Main mineralogy: Kaolinite $Al_2(Si_2O_5)(OH)_8$ Silica SiO_2
Average analyses of Kaolin

SiO_2	50.00%
Al_2O_3	35.00
Fe_2O_3	0.40
TiO_2	0.05
CaO	tr.
MgO	0.20
alkalies	tr.
L.O.I.	13.00

Besides kaolin there were minor quartz inclusions (≤ 5%) and talc and mica (≈1%). Figure 9.19 shows the material. Some of the powder was sized using a set of ASTM standard sieves manufactured by Endecotts Ltd., London, England. The measured weight percentages retained in each sieve are listed in Table 9.10 and are shown graphically on Figure 9.20a.

Microwaved material

About 50 g of kaolin was heated in a 1.4 kW microwave oven for 2 minutes and 20 minutes. After 2 minutes the temperature had reached 107°C. The temperature after 20 minutes was not measured. The powder was again sieved and the results are given on Table 9.10 and on Figure 9.20b. There were no visible changes between the microwaved and as-received material.

Table 9.10
Sieve Size Results for Kaolin Sample After Shaking for 0.5 h

			% Weight Retained	
	Sieve Size		As-received	Microwaved
A	4.00	mm	40.20	45.49
B	2.80	mm	7.44	5.89
C	2.00	mm	8.20	6.44
D	1.40	mm	7.44	6.40
E	1.00	mm	5.72	5.85
F	710	µm	4.61	4.58
G	500	µm	4.00	3.27
H	300	µm	2.70	2.80
I	212	µm	2.01	1.89
J	125	µm	13.63	8.81
K	75	µm	2.52	7.47
L	25	µm	0.51	1.30
	<25	µm	0.06	0.08

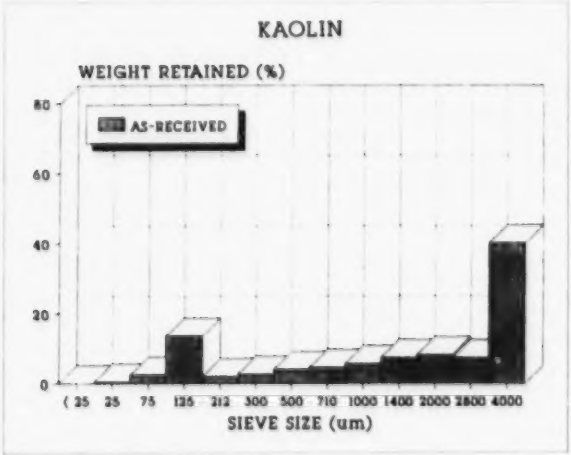


Figure 9.20a
Particle size distribution of as-received kaolin.

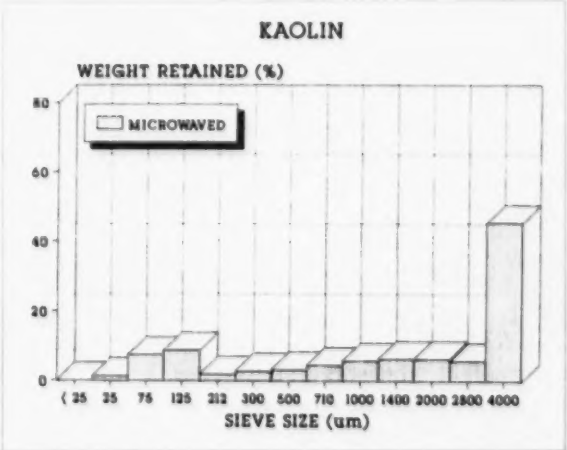


Figure 9.20b
Particle size distribution of microwaved kaolin.

Microscopic examination

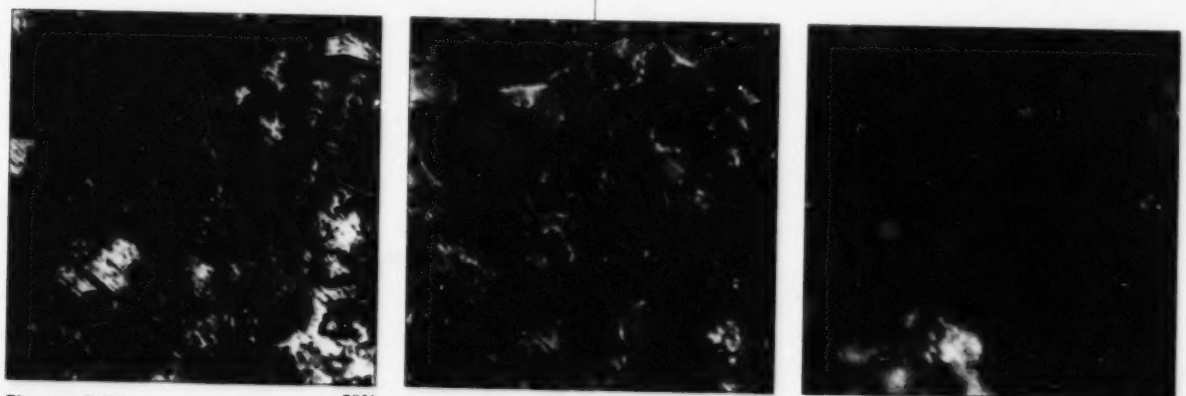
A microscopic examination was made of both as-received powder and powder which had been heated in a laboratory furnace to 800°C for 15 minutes. 800°C was chosen because it was the maximum temperature at which the dielectric constant was to be measured. The temperature should also produce any irreversible chemical changes that may be expected, as predicted above. The heat treatment changed the colour of the material from white to a light brown.

Figure 9.21 shows the as-received material. Material heated to 800°C is shown in Figure 9.22. There is no obvious structural difference between the two.

Dielectric measurements

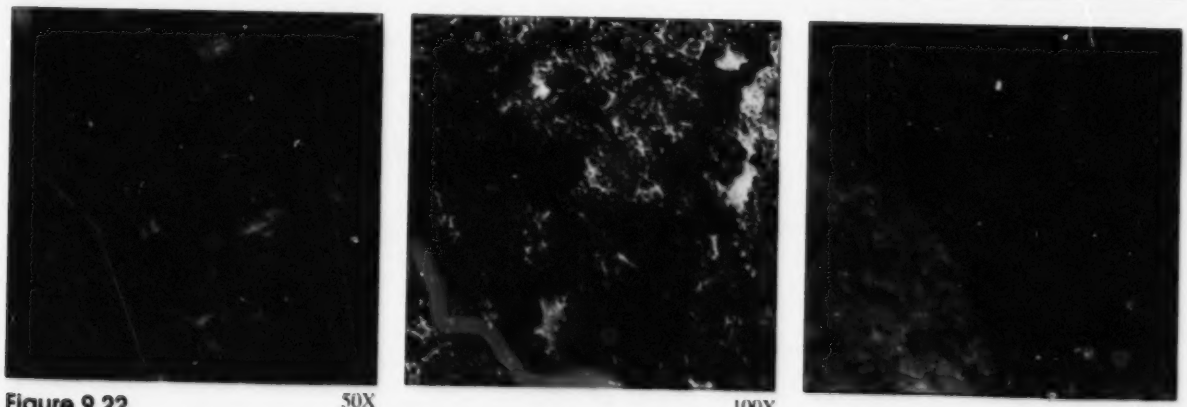
Measurements were done on several different samples at room temperature, at successively higher temperatures up to 800°C, during cooling from 800°C and on samples from previous tests (furnace heated to 800°C). The results are listed in Table 9.11.

Since different specimens were used, sample variation between tests resulted in variation in the measured dielectric constants. To compensate, all measurements were normalized to a nominal specimen density of 1.25 g/mL. This value was arbitrarily selected as being about the mid-range of the sample densities used. The normalized values of ε' and ε'' are listed in Table 9.11 and plotted on Figures 9.23 and 9.24.



50X 100X 400X

Figure 9.21
Photomicrographs of as-received kaolin.



50X 100X 400X

Figure 9.22
Photomicrographs of kaolin heated to 800°C for 15 minutes.

Table 9.11
Dielectric Measurements for Kaolin, As-Measured and Normalized+ to a Density of 1.25 g/ml

Temperature °C	Density g/mL	ε'		ε"	
		Measured	Normalized+	Measured	Normalized+
Room	1.22	2.77	2.81	0.196	0.201
	1.31	2.93	2.84	0.125	0.119
	1.29	2.73	2.68	0.138	0.134
*	1.10	2.20	22.36	0.0064	0.0073
110	2.17	0.080			
200	2.09	0.0068			
400	2.04	0.00546			
800	1.96	0.0115			
Cooling curve					
750	1.25	2.11	2.11	0.0121	0.0121
700	1.25	2.08	2.08	0.0087	0.0087
600	1.25	2.01	2.01	0.0060	0.0060
500	1.25	1.95	1.95	0.0046	0.0046
400	1.25	1.91	1.91	0.0039	0.0039
300	1.25	1.87	1.87	0.0033	0.0033
200	1.25	1.85	1.85	0.0030	0.0030
100	1.25	1.82	1.82	0.0028	0.0028
50	1.25	1.82	1.82	0.0030	0.0030

+ Normalized is linear with density for $(1-\varepsilon')$ and ε''.

* Heated to 800°C cooled to room temperature and measured.

The real portion of the dielectric constant, ε', is weakly temperature dependent. The cooling curve is about 50% lower than the heating curve, suggesting that the heating cycle has resulted in physical and/or chemical changes, as expected. The imaginary portion of the dielectric constant, ε", shows this more clearly. Heating to 200°C resulted in a dramatic drop in ε", probably caused by drying of absorbed moisture. There was a further small drop to 400°C and then ε" increased to 800°C. The cooling curve showed a continuous decrease in ε" with temperature from 800°C to 100°C but below this the value started to rise, possibly by as much as a factor of 2 between 100°C and room temperature. The difference of nearly a factor of 20 between the room temperature measurements of as-received and heated to 800°C samples confirms that considerable chemical/physical change has occurred.

Conclusions

Kaolin was found to interact only moderately with microwaves. A sample irradiated in a microwave oven for 2 minutes reached a temperature of 107°C.

Both real and imaginary components of the dielectric constant were measured during heating and cooling between room temperature and 800°C. Heating to 800°C produced chemical/physical changes such that the dielectric constant during cooling was significantly different from that during heating.

Microwaving kaolin for 20 minutes in a 1.4 kW microwave oven produced no change in colour or in particle size.

Recommendations

Kaolin which has been heated to 800°C has a low dielectric constant. The imaginary portion of the dialectric constant ε" is of the order of 0.005. Even increasing the density a factor of 2 still gives low microwave absorption. Therefore, fired material should be tested in order to determine its response to microwave fields.

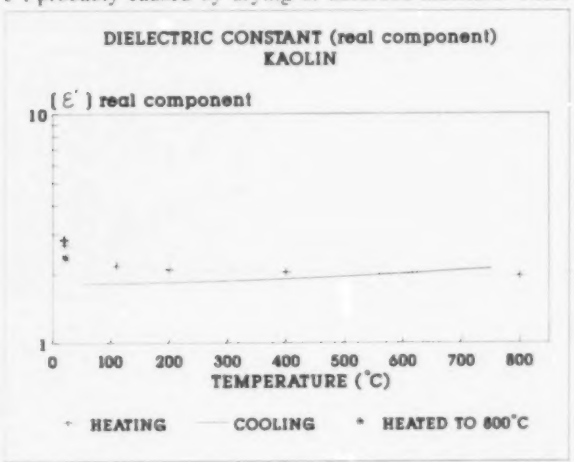


Figure 9.23
Real component of dielectric constant for kaolin during heating to, and cooling from 800°C.

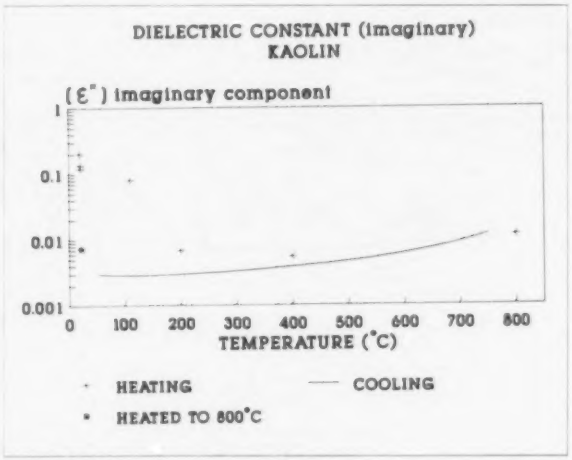


Figure 9.24
Imaginary component of dielectric constant for kaolin during heating to, and cooling from 800°C.

9.6 Vermiculite

Summary

A vermiculite sample was received from Cargill Township, in Northern Ontario, in the form of a coarse powder with many large pieces. Heating, either in a laboratory oven or by microwaves, caused exfoliation. Microwave powers ranging from 1.4 to 5 kW had no effect on the degree of exfoliation, i.e. the higher input energy did not cause explosive boiling of the interlayer water. In fact the ratio of exfoliation, ranging from 3 to 13, measured with this material appears to be low compared with values of up to 30 quoted in the literature [92].

Measurements of the dielectric constants as a function of temperature were complicated by exfoliation, because the values measured depend on density. The sample of small particles was heated slowly, minimizing the exfoliation, and tamped to recompress when sample expansion occurred. As observed in other materials, there is a difference in the imaginary component, ε", of the dielectric constant of an order of magnitude at room temperature between "wet" and "dry" vermiculite.

Expected Behaviour

Vermiculite is a layered structure with water molecules (as H_2O) between the layers. These can be driven off by heat. OH^- ions will be driven off at temperatures somewhere above 300°C. If heating to 300°C is rapid, the H_2O molecules convert to steam and cause exfoliation of the layered structure. If heating is slow, the H_2O is driven off without disrupting the structure.

Experimental Results

Sample as-received

Vermiculite as a coarse brown powder was supplied by the Ministry of Northern Development and Mines. No specific chemical analysis was provided. The nominal chemical composition of vermiculite is:

$$(Mg, Ca)_{0.7} (Mg, Fe^{+3}, Al)_{6.0} [Al, Si)_8O_{20}] (OH)_4.8H_2O$$

A sample of the material was sized using a set of ASTM standard sieves manufactured by Endecotts Ltd., London, England. The measured weight percentages retained in each sieve are listed in Table 9.12 and are shown graphically on Figure 9.25

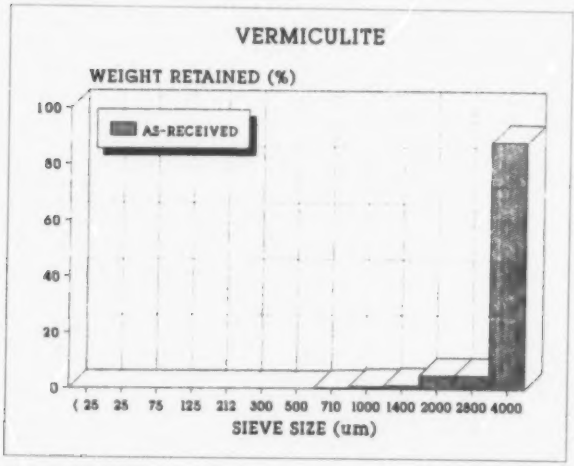


Figure 9.25
Particle size distribution of as-received vermiculite.

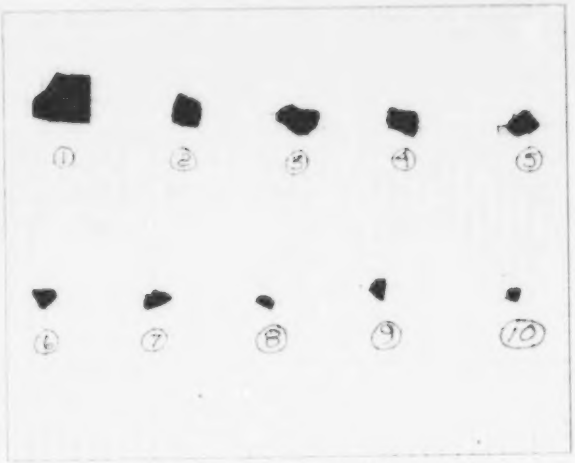
Table 9.12
Sieve Size Results for Vermiculite Sample After Shaking for 0.5 h

	Sieve Size		% Weight Retained
A	4.00	mm	88.23g
B	2.80	mm	4.74 g
C	2.00	mm	4.71 g
D	1.40	mm	1.22 g
E	1.00	mm	0.79 g
F	710	µm	0.30 g
G	500	µm	0
H	300	µm	0
I	212	µm	0
J	125	µm	0
K	75	µm	0
L	25	µm	0
	<25	µm	0

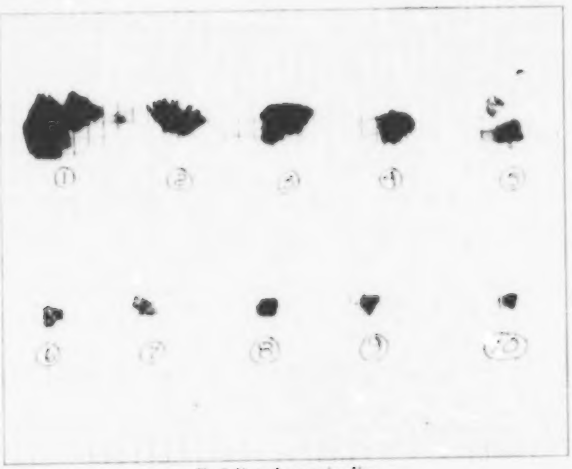
Microwave treated material

Some vermiculite was heated in a 1.4 kW microwave oven for 2 minutes. Considerable exfoliation occurred which made temperature measurement difficult. 171°C was the highest value recorded after the two minutes.

Samples of various sizes were selected and heated for three minutes in a microwave cavity using 5 kW microwave power input. This is the highest power we had available. The thickness of each sample (c axis dimension) was measured both before and after testing. Samples were soaked in water for a few minutes to ensure that the smallest samples had not dried out. The range of samples used are shown on Figure 9.26 and the dimensional changes listed on Table 9.13. There was no correlation between sample size and the degree of exfoliation. Exfoliation ratios varied from less than 3 to over 13, with an average of 6 times. This seems low compared with the 30 times expansion quoted in Reference 92. In order to obtain explosive exfoliation (and therefore the potential for greater expansion) much higher energy deposition rates, and hence higher powered microwave sources, would be required.



As received vermiculite



Exfoliated vermiculite

Figure 9.26. Comparison between as-received vermiculite and the same particles exfoliated using microwave power.

Table 9.13
Exfoliation of Vermiculite After 3 Minutes at 5 kW Microwave Power

Sample #	Original Thickness (mm)	Post-Microwave Thickness (mm)	Ratio Post-Microwave Original
1	2.19	15.97	7.29
2	1.84	24.96	13.56
3	6.05	22.84	3.77
4	1.28	14.78	11.54
5	3.92	10.59	2.70
6	1.33	4.73	3.55
7	0.77	4.07	5.28
8	1.86	8.49	4.56
9	1.23	5.57	4.52
10	1.53	5.01	3.27
		Average	6.00

Microscopic examination

Microscopic examination was attempted on both as-received and exfoliated vermiculite. No difference was detected and photography was unsatisfactory due to difficulties in focusing a sufficiently large field of view.

Dielectric measurements

Measurements were done on several different samples at room temperature, at successively higher temperatures up to 700°C and on samples from previous tests (furnace heated to 800°C). The results are listed in Table 9.14.

Table 9.14
Dielectric Measurements for Vermiculite, As-Measured and Normalized+ to a Density of 2.00 g/mL

Temperature °C	Density g/mL	ε'		ε"	
		Measured	Normalized+	Measured	Normalized+
Room	2.05	8.629	8.44	0.771	0.752
	1.76	10.2	11.45	1.19	1.35
	1.61	5.30	6.34	0.60	0.745
*	1.14	1.66	2.16	0.0859	0.151
110	2.05**	4.92	4.82	1.129	1.102
200	1.45x	3.5	4.45	0.32	0.44
300	1.45x	3.01	3.77	0.201	0.28
400	1.45x	3.36	4.25	0.331	0.46
500	1.45x	3.65	4.66	0.439	0.60
600	1.45x	4.74	6.16	0.402	0.55
700	1.45	4.78	6.21	0.348	0.48

+ Normalization for (ε'-1) and ε" is linear with density.
* Measured at room temperature after heating sample to 800°C.
** Density at start of test.
x Density after testing to 700°C.

Since different specimens were used, sample variation between tests resulted in variation in the measured dielectric constants. To compensate, all measurements were normalized to a nominal specimen density of 2.00 g/mL. This value was arbitrarily selected. Both (ε'-1) and ε'' vary linearly with density. The normalized values of ε' and ε'' are listed in Table 9.14 and plotted on Figures 9.27 and 9.28.

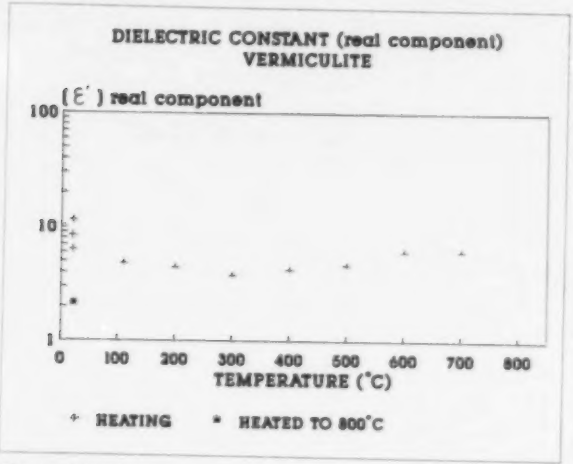


Figure 9.27
Real component of dielectric constant for vermiculite during heating to, and cooling from 800°C.

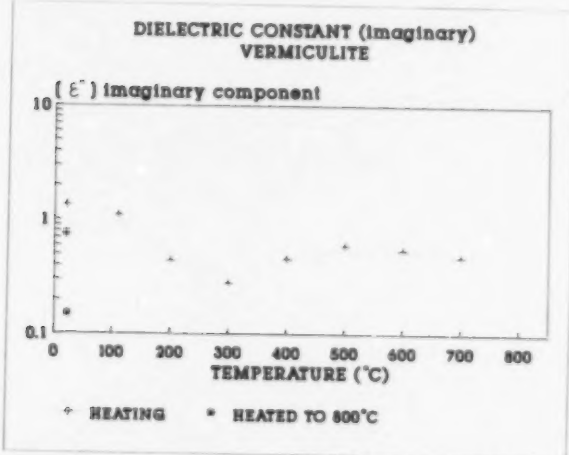


Figure 9.28
Imaginary component of dielectric constant for vermiculite during heating to, and cooling from 800°C.

Both the real and imaginary parts of the dielectric constant show a significant decrease with temperature, up to 300°C, as water is driven off. Both then increase up to about 500° or 600°C and then level out. The one measurement taken at room temperature on material which had previously been heated to 800°C lies on a reasonable extrapolation of the heating curve above 300°C, suggesting that above this temperature the heating and cooling curves may be similar. Cooling curves were not made on this material because of difficulties in maintaining a uniform density over the temperature range. This problem could be overcome with small changes in experimental technique.

The above results suggest that the major physical/chemical change was the elimination of interlayer H_2O. Elimination of bound water, in the form of (OH^-), could not be confirmed. More extensive measurements, including a cooling curve, would be required.

Conclusions

The vermiculite supplied for this work interacted only moderately with low-power microwaves. Exfoliation occurred but the maximum temperature reached was less than 200°C. Higher power microwaves (5 kW) caused exfoliation with an expansion ratio varying between about 3 and 13.5 times. This is significantly less than the 30 times quoted in the literature [92].

Recommendations

Future work should include measurements of the dielectric constant during cooling to determine if bound water is driven off by heating to 800°C.

Small pieces of vermiculite seem to have dried out in the laboratory. Soaking briefly in water partially restored the exfoliation behaviour on heating. Optimum conditions for rehydration should be investigated.

9.7 Magnetite

Summary

Material labelled "magnetite concentrate," from Indusmin Division of Falconbridge Ltd., Nephton, Ontario, consisted of a black, fine-grained, free-flowing powder. No changes were detected from heating this material to 800°C, nor was any expected. A sample heated in a 1.4 kW microwave oven heated rapidly, reaching 730°C in two minutes. Thus, magnetite readily absorbs microwaves.

Dielectric measurements were made at temperatures up to 1000°C. The real part of the dielectric constant, ε', increased by less than a factor of 2 over this temperature range. The imaginary part, ε'', which is a good indicator of absorption of the electrical field component of the microwave signal, increased by a factor of 30. If the room temperature measurement of a sample previously heated to 800°C represents the effect of absorbed moisture in the powder, then drying decreases the room temperature ε'' by a factor of 3 giving a 90 fold increase in ε'' between dry powder at room temperature and at 1000°C.

Although the dielectric constant was of the same order of magnitude as the other materials tested in this work, the temperature rise measured in the microwave oven suggested much more energy was being absorbed from the microwave field. Since magnetite is a magnetic material, a measurement was made of the complex magnetic permittivity during cooling from 800°C. The imaginary component, μ", was relatively constant, dropping about a factor of 3 above the curie point, the transition occurring over a temperature range from about 500° to 630°C. The curie point for pure magnetite is 578°C [92].

Expected Behaviour

Magnetite is the most common mineral which is known to be a hyperactive microwave susceptor: as a "thermal seed", it is referred to in all the mineral and ore microwave heating and microwave diagnostic literature. Data exist but they are inadequate at high temperatures for the evaluation of claims made for its potential use in processing materials.

Magnetite is the stable oxide in air at temperatures above 1388°C. Haematite is the stable form below this temperature. Thus, heating to 800°C or higher may cause some conversion from magnetite to haematite. However, given the general sluggishness of many phase transformations in oxide systems and including the requirement that the magnetite oxidize to accomplish the transformation, it is probable that in the time frame of these experiments there will be little structural change.

Experimental Results

Sample as-received

A sample of fine grained free flowing sand, black in colour with some white grains, labelled "magnetite concentrate" was supplied by the Ministry of Northern Development and Mines. A chemical analysis, provided by the Ministry is given in Table 9.15.

Table 9.15
Chemical Analysis of Magnetite Sample

Magnetite -	Fe assay = 60.7% (83.2% Fe_2O_3) The balance would be primarily nepheline syenite.	
Nepheline Syenite 340 (typical analyses)	Fe_2O_3	0.10%
	Al_2O_3	23.8
	Na_2O	10.4
	K_2O	4.8
	CaO	0.4
	MgO	0.04
	L.O.I.	0.3
	SiO_2	60.5 (by difference)

Some of the sand was sized using a set of ASTM standard sieves manufactured by Endecotts Ltd., London, England. The measured weights retained in each sieve are listed in Table 9.16 and are shown graphically on Figure 9.29.

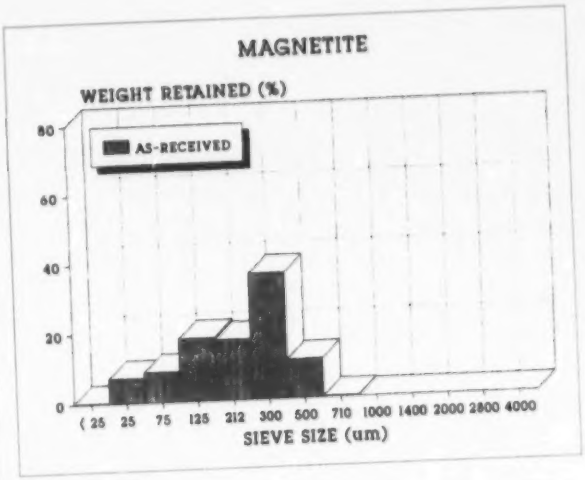


Figure 9.29
Particle size distribution of as-received magnetite.

Table 9.16
Sieve Size Results for Magnetite Sample After Shaking for 0.5 h

	Sieve Size	% Weight Retained
A	4.00 mm	0
B	2.80 mm	0
C	2.00 mm	0
D	1.40 mm	0
E	1.00 mm	0
F	710 μm	0.23
G	500 μm	11.07
H	300 μm	36.17
I	212 μm	17.41
J	125 μm	18.05
K	75 μm	8.74
L	25 μm	7.11
	<25 μm	0.24

Microwave treated material

About 35 g of powder was irradiated in a 1.4 kW microwave oven for two minutes. The temperature was measured by inserting a thermocouple immediately after the oven turned off. The maximum temperature measured after two minutes was 728°C. No visible changes occurred to the sample and no longer irradiation was done. The sample's magnetic characteristics appeared to be unchanged.

Microscopic examination

Microscopic examination was made of both as-received powder and a sample which had been heated in a laboratory furnace to 800°C for 15 minutes. A temperature of 800°C was chosen as the maximum temperature for the dielectric constant measurements described in the next section. In fact, dielectric measurements were made up to 1000°C.

Figures 9.30 and 9.31 show photomicrographs of as-received and heated material respectively. No difference could be determined as a result of the heat treatment.

Dielectric Measurements

Measurements were done on several different samples at room temperature, at successively higher temperatures up to 1000°C, and on a sample previously heated to 800°C. The results are listed in Table 9.17.

Table 9.17
Dielectric Measurements for Magnetite, As-Measured and Normalized+ to a Density of 2.90 g/mL

Temperature °C	Density g/mL	ε' Measured	ε' Normalized+	ε'' Measured	ε'' Normalized+
Room	2.84	8.838	9.02	0.082	0.084
	2.81	8.72	9.00	0.089	0.092
*	2.81	9.37	29.67	0.028	0.029
110	2.90	8.717	8.717	0.0806	0.0806
150	2.90	8.735	8.717	0.0806	0.0806
200	2.90	8.759	8.759	0.0816	0.0816
400	2.90	8.935	8.935	0.148	0.148
600	2.90	9.587	9.587	0.388	0.388
800	2.90	10.71	10.71	1.108	1.108
1000	2.90	14.96	14.96	2.74	2.74
		μ' Measured	μ' Normalized	μ'' Measured	μ'' Normalized
Room	2.70	0.0964	0.104	0.669	0.719

+ The effect of density is assumed linear for (ε'-1) and ε''.

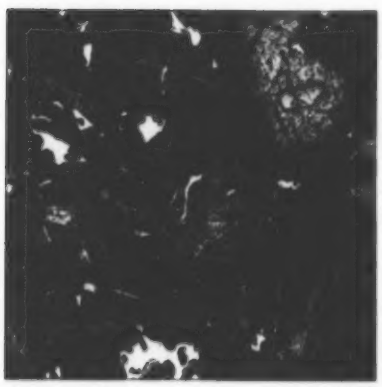


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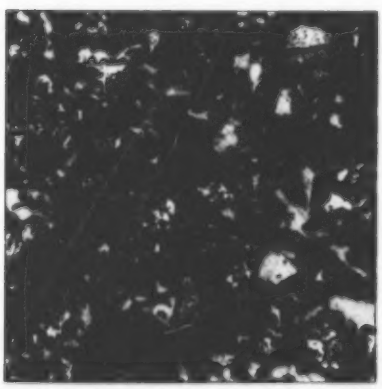
Figure 9.30
Photomicrographs of as-received magnetite.



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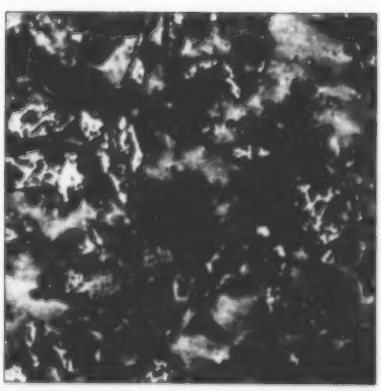

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Figure 9.31
Photomicrographs of magnetite heated to 800°C for 15 minutes.

Since different specimens were used, sample variation between tests resulted in variation in the measured dielectric constants. To compensate, all measurements were normalized to a nominal specimen density of 2.90 g/mL. This value was arbitrarily selected. Both (ε'-1) and ε'' vary linearly with density. The normalized values of ε' and ε'' are listed in Table 9.17 and plotted on Figures 9.32 and 9.33.

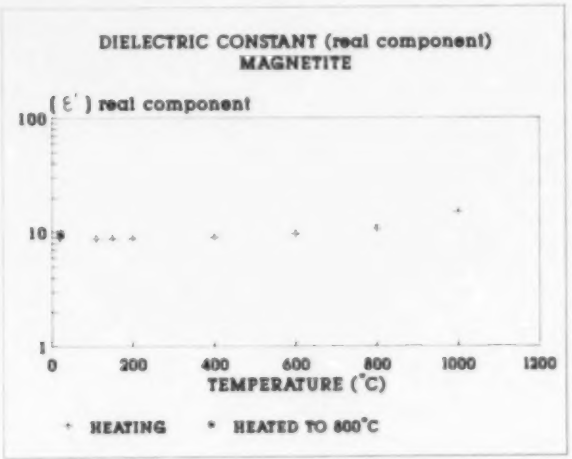


Figure 9.32
Real component of dielectric constant for magnetite during heating to 1000°C.

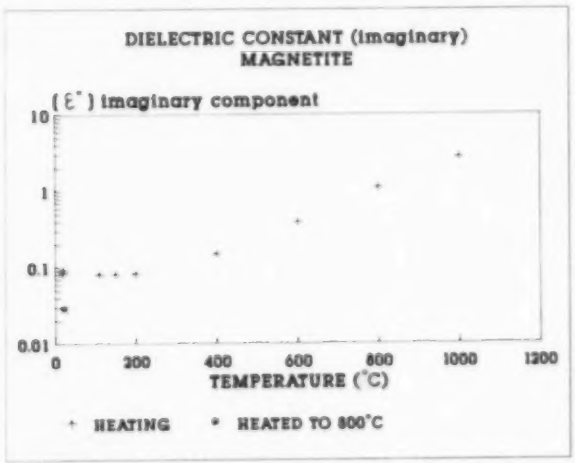


Figure 9.33
Imaginary component of dielectric constant for magnetite during heating to 1000°C.

The real component of the dielectric constant is almost independent of temperature up to about 500 °C, increases slowly up to 800°C and rapidly between 800° and 1000°C. The imaginary component is temperature independent up to 200°C but then becomes very sensitive to temperature, increasing 1.5 decades between 200° and 1000°C. The sample which was re-measured at room temperature after heating in air in a laboratory furnace to 800°C had a very much lower value of ε'' than unheated material, one that almost lies on an extrapolation of the high temperature sector of the curve. This suggests that some chemical change may have occurred during the heating cycle but on the other hand the initial behaviour up to 200°C may indicate moisture absorbed on the concentrate. Further measurements should be done on material which has been carefully dried in order to clarify this point.

The loss tangent is defined as the ratio $\varepsilon''/\varepsilon'$. Low values of the loss tangent indicate low losses in the material. The room temperature loss tangent for this magnetite is low, about 0.01. It is therefore surprising that the material heated so quickly in a microwave oven. A single measurement was made at room temperature of the complex magnetic permittivity. The values of μ' and μ'' are given on Table 9.17. The ratio μ''/μ' is about 7.5.

Thus, the room temperature microwave losses in magnetite are caused primarily by absorption of the magnetic component of the microwave field rather than absorption of the electric component of the field.

Conclusions

The "magnetite concentrate" tested in this work interacted strongly with a microwave field. After two minutes in a 1.4 kW microwave oven a 35 g sample reached about 730°C.

Both the real and imaginary components of the dielectric constant were measured from room temperature up to 1000°C. Room temperature measurements of as-received and heated material suggest that the as-received sample contained absorbed water.

The room temperature interaction of the sample with the electric field component of the microwave radiation was small. The major microwave absorption at this temperature was from the magnetic field component of the microwave radiation.

Recommendations

Additional measurements should be made to determine if the low temperature (below 200°C) behaviour of ε'' was due to absorbed moisture.

Since the complex magnetic permittivity dominates magnetite's microwave absorption at room temperature, measurements of the temperature dependence of μ_0 should be made.

9.8 Talc

Summary

Talc was supplied in the form of a fine grained white powder. The "FDC" grade product came from Luzenac Inc., Timmins, Ontario and product "E" from National Silicates Limited, Toronto, Ontario. Microwaving for 20 minutes in a 1.4 kW oven only raised the temperature to 122°C; however, it did appear to reduce the particle size. This could have been the result of evaporating absorbed water, which could have made the as-received grains stick together.

Heating talc to 800°C is expected to decompose it to enstatite and silica and give off water derived from OH^- ions. There was no visual change observed nor was any change apparent on microscopic examination.

The imaginary component of the dielectric constant, ε", is very sensitive to small changes in a material. On heating, the values of ε" are about a factor of 2 higher than those measured during cooling on another sample. This difference may indicate a real change caused by the thermal decomposition mentioned above. However, all the values of ε" are very low and this difference may reflect the precision to be expected when measuring such low values. Additional work would be required to resolve this point.

Addition of binder to the talc raised the room temperature value of ε" over an order of magnitude. This was expected since the binder was liquid sodium silicate. Heating to 200°C dried the water and the measured ε" was the same as for pure talc. However, on further heating the talc plus binder had higher and higher values of ε" compared with the pure talc at the same temperatures. This effect is presumably caused by the introduction of sodium silicate into the magnesium silicate (enstatite) and silica mixture, but the mechanism is not known. The properties of pure sodium silicate should be measured.

Talc has the lowest microwave absorption of any of the materials tested in this work. It may be worthwhile investigating its potential use for fabrication of components for microwave circuitry.

Expected Behaviour

In pure, dry form, talc is considered to be inert to microwaves below 900°C; bound water, chlorite, magnetite, pyrite will affect the response. Talc decomposes on heating to enstatite, silica, and water according to the equation:

$$Mg_3 Si_4 O_{10} (OH)2 \rightarrow 3\ Mg\ Si\ O_3 + Si\ O_2 + H_2O$$

Elimination of the bound water (OH^- ions) should change the microwave response compared with as-received material.

A second material, a binder labelled "product E" (sodium silicate) was provided. This is a water soluble "glass". The effect of a small quantity of this material on the dielectric constants for talc were to be measured. Since the binder contains water, considerable low temperature response was expected.

Experimental Results

Sample as-received

A sample of fine, white powder labelled "Talc" was supplied by the Ministry of Northern Development and Mines. A chemical analysis, provided by the Ministry, is given in Table 9.18.

Table 9.18
Chemical Analysis of Talc Sample

SiO_2	61-62%
MgO	31-32
Fe_2O_3	1.3
CaO	0.7
Al_2O_3	0.1
Loss on Ignition (LOI)	5.5

Some of the powder was sized using a set of ASTM standard sieves manufactured by Endecotts Ltd., London, England. The measured weights retained in each sieve are listed in Table 9.19 and are shown graphically on Figure 9.34a.

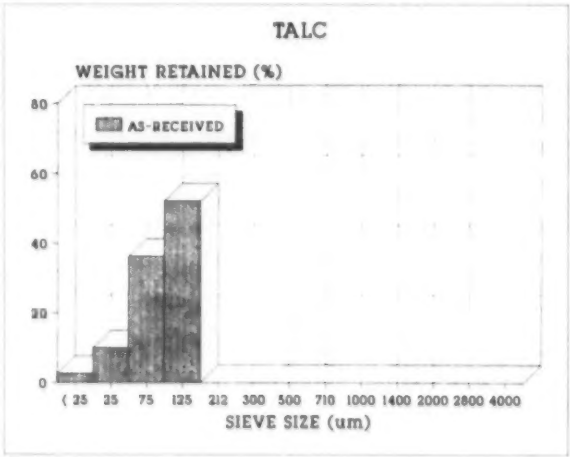


Figure 9.34a
Particle size distribution of as-received talc.

Table 9.19
Sieve Size Results for Talc Sample After Shaking for 0.5 h

	Sieve Size		% Weight Retained As-received	Microwaved
A	4.00	mm	0	0.10
B	2.80	mm	0	0.07
C	2.00	mm	0	0.05
D	1.40	mm	0	0.10
E	1.00	mm	0	0.06
F	710	µm	0	0.04
G	500	µm	0	0.12
H	300	µm	0	0.09
I	212	µm	0	0.14
J	125	µm	52.08	0.33
K	75	µm	36.12	50.00
L	25	µm	9.89	47.88
	<25	µm	2.50	1.02

Microwaved material

About 35g of powder was heated for 2 minutes and 20 minutes in a 1.4 kW microwave oven. Heating for two minutes raised the bulk temperature to 78°C, 20 minutes raised it to 122°C. There was no visible change. The microwaved material was again sieved and the results are given on Table 9.19 and Figure 9.34b. There was an apparent decrease in particle size by one sieve size. This is most likely the result of drying the powder during the 20 minutes in the microwave oven.

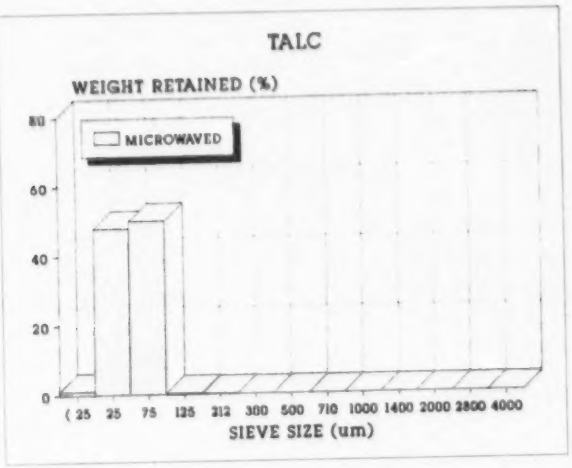


Figure 9.34b
Particle size distribution of microwaved talc.

Microscopic examination

Microscopic examination was done on as-received material and on a sample which had been heated in a laboratory furnace to 800°C for 15 minutes. 800°C was chosen as the maximum temperature for the dielectric constant measurements described in the next section. This temperature was also expected to produce the predicted chemical change described above.

Figure 9.35 shows micrographs of the as-received material and Figure 9.36 shows the heated material. No obvious physical changes were apparent.

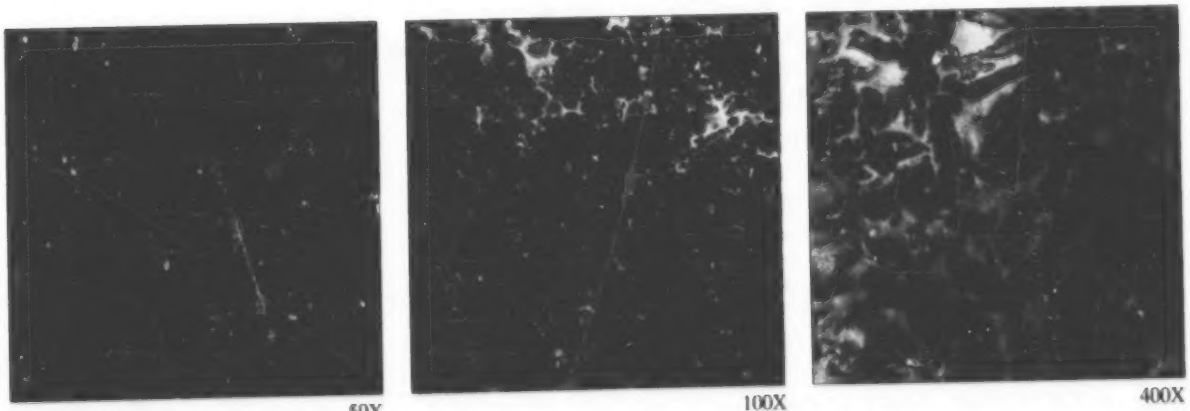
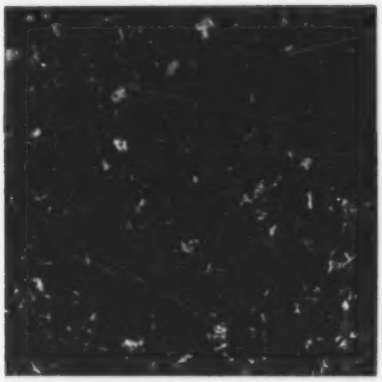
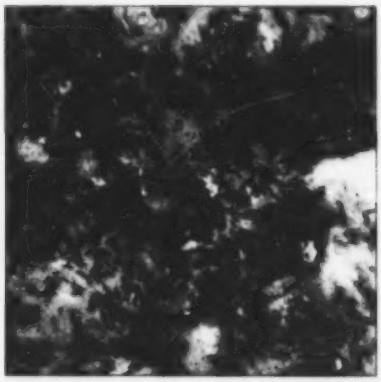


Figure 9.35
Photomicrographs of as-received talc.

50X



100X



400X

Figure 9.36
Photomicrographs of talc heated to 800°C for 15 minutes.

Dielectric Measurements

Measurements were done on several different samples at room temperature, at successively higher temperatures up to 800°C, during cooling from 800°C and on samples from previous tests (furnace heated to 800°C and microwaved for 20 minutes). The results are listed in Table 3.8.3.

Table 9.20
Dielectric Measurements for Talc, As-Measured and Normalized+ to a Density of 1.20 g/mL

Temperature °C	Density g/mL	ε'		ε"	
		Measured	Normalized+	Measured	Normalized+
10	1.15	2.08	2.13	0.00119	0.0012
Room	1.19	2.13	2.14	0.00408	0.0041
	1.12	2.03	2.10	0.00193	0.0021
*	1.12	2.03	22.10	0.00086	0.00092
110	1.33	2.23	2.01	0.0029	0.0026
200	1.33	2.23	2.01	0.0035	0.0032
400	1.33	2.21	1.99	0.0035	0.0032
800	1.33	2.43	2.19	0.0103	0.0093
Cooling curve					
800	1.16	1.89	1.92	0.0048	0.0050
700	1.16	1.84	2.87	0.0029	0.0030
600	1.16	1.80	1.83	0.0020	0.0021
500	1.16	1.77	1.80	0.0018	0.0019
400	1.76	1.74	1.76	0.0016	0.0016
300	1.16	1.72	1.74	0.0013	0.0013
200	1.16	1.70	1.72	0.0011	0.0011
100	1.16	1.69	1.71	0.0010	0.0010
50	1.16	1.68	1.70	0.0009	0.0009

+ Normalization is linear with density for (1-ε') and ε".
* Measured after heating sample to 800°C.

Since different specimens were used, sample variation between tests resulted in variation in the measured dielectric constants. To compensate, all measurements were normalized to a nominal specimen density of 1.20 g/mL. This value was arbitrarily selected as being about the mid-range of the sample densities used. Both (ε'-1) and ε" vary linearly with density. The normalized values of ε' and ε" are listed in Table 9.20. Those for the talc mixed with binder are listed on Table 9.21. Both sets of results are plotted on Figures 9.37 and 9.38.

Table 9.21
Dielectric Measurements for 95% Talc + 5% Binder, As-Measured and Normalized+ to a Density of 1.20 g/mL

Temperature °C	Density g/mL	ε'		ε"	
		Measured	Normalized+	Measured	Normalized+
Room	1.20	2.27	2.27	0.0333	0.0333
*	0.93	1.95	22.23	0.00186	0.0024
110	1.10	2.07	2.17	0.00436	0.00476
200	1.10	2.04	2.13	0.00269	0.00293
400	1.10	2.02	2.11	0.00350	0.00382
800	1.10	2.23	2.34	0.0241	0.0263
1000	1.10	2.41	2.54	0.0787	0.0858

+ Normalization is linear with density for (ε'-1) and ε".
* Sample measured after heating to 1000°C.

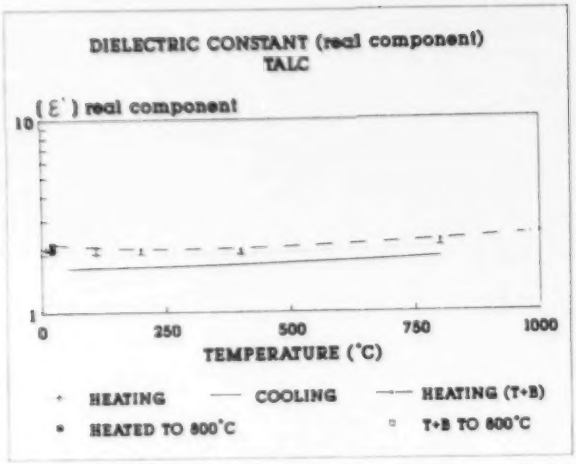


Figure 9.37
Real component of dielectric constant for talc and talc +5% binder during heating and cooling.

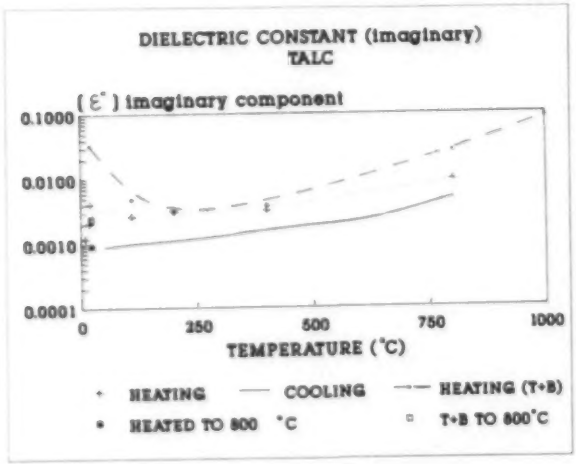


Figure 9.38
Imaginary component of dielectric constant for talc and talc +5% binder during heating and cooling.

The real component of the dielectric constant, ε', for both talc and talc + binder was relatively insensitive to temperature up to 400°C. Above this temperature there was a small increase. The imaginary component, ε", shows considerable temperature dependence over the whole range. Two features should be noted. First, the heating and cooling curves for ε" are offset by about a factor of 2. A similar but smaller offset occurs in the ε' results. Second, three room temperature measurements on three different samples give results differing by a factor of about 3.4. This amount of scatter would normally be of concern. However, it is possible that at these low absolute values, of the order of 10^{-3}, greater precision may not be possible. This would suggest that the difference between the heating and cooling curve may not exist except for the difference measured for ε's, which should not suffer from the same difficulties. If experimental scatter does not explain the difference, then the materials being heated and cooled are different. This suggests that the chemical conversion of talc to enstatite plus silica was occuring while the cooling test sample was at temperature. If this is the case, was the reaction complete? Further work would be required to answer these questions.

The ε" results for talc with 5% binder show the expected dominance of the water in the binder at room temperature. By 200°C this is driven off and between 200° and 400°C the binder shows little effect beyond that measured for pure talc. However, at 800°C, ε" for the talc plus binder is a factor of 3 higher than than talc alone. Whether this is a mixture effect or the sodium modifies the enstatite structure is open to conjecture. Further experiments involving differing amounts of binder, and cooling curves after sufficient time at high temperature to ensure completion of the chemical changes, should be considered.

Conclusions

The talc tested in these experiments interacted only slightly with microwaves. A sample irradiated for 20 minutes in a 1.4 kW microwave oven only reached a temperature of 122°C.

Both the real and imaginary portions of the dielectric constant were measured during heating and cooling over the range from room temperature to 800°C. Talc with 5% binder (product E) was measured up to 1000°C.

Both the real and imaginary portions of the dielectric constant differed between heating and cooling, including a marked offset between the two curves at 800°C. It was not determined if this difference was the result of the chemical change from talc to enstatite and silica, or represented experimental difficulties.

Recommendations

Further work should be done to confirm the difference in dielectric constant between heating and cooling curves.

If the difference above is real, the kinetics of the presumed chemical change should be determined. If the reaction is slow and was not completed in these tests it is possible we may find a material with even lower ε''. Such materials may be of use in microwave circuits or components.

The effect of various amounts of binder both during heating and after the chemical transformation should be examined. The combination of binder and thermally transformed talc may make possible tailoring of the dielectric constant over a considerable range.

References and Notes

Notation: references are cited in the text within square brackets and listed here. The designation in the text (for example) [11:110] refers to page 110 of reference 11. An asterisk (*) indicates sources consulted and information received during May 1989.

1 Langman, R.D. 1987. Worked Examples in Electroheat; British National Committee for Electroheat (BNCE)-Electricity Council, London, p.19 ISBN 0.85188.111.4. An important educational text for all aspects of industrial electroheat.

2 BNCE. 1983. **Dielectric heating for industrial processes**; UK Electricity Council, 30 Millbank, London SW1P 4RD, 30 p.

3 Sutton, W.H., Brooks, M.H. and Chabinsky, I.J. eds. 1988. **Microwave Processing of Materials;** Materials Research Society Symposium Proceedings 124 (Reno Nevada, April 1988) See, in particular, Chabinsky, I.J., Bruce, R.W. p. 3-31.

4 Sanio, M.R. 1987. (A) **Microwave applications in the food and beverage industry**; Ontario Hydro Industrial Product Development Division, Toronto, p. 31. (includes appendices with names and addresses of equipment suppliers, testing facilities etc.) (B) Sanio, M.R. and Schmidt, P.S. 1988 *in* [3] p. 337-346.

5 Jones, P.L. 1988. A decade of experience in the development and commercialization of industrial dielectric heating applications; EPRI Conference paper records; *in* Electromagnetic Energy Reviews March 1989, v.2, no. 1, p. 9-13.

6 Metaxas, A.C. and Meredith, R.J. 1983. **Industrial Microwave Heating**; IEE Monograph Power Engineering Series #4, Peter Peregrinus, London, p. 299-319.

7 Gerling Laboratories. **A listing of microwave patents associated with industrial processing and domestic/commercial ovens**; (To May 1986, updates available. Updates also published 1988, 1989 in Electromagnetic Energy Reviews.).

8 Voss, W.A.G. ed. 1987. International Microwave Power Institute **Index**, Volume 1 (1966-1979) and Volume 2 (1980-1986); IMPI, Clifton VA, 2x75p. (Historical and subject-order listing, 1980f with abstracts of all papers in Journal of Microwave Power, IMPI Proceedings, short courses and Newsletters, since 1966).

9 Microdry Corporation. 1988. Various literature at September 1988 Microwave Power Symposium, Ottawa. (Microdry Corporation, 1745 Highway 329, Crestwood KY 40014).

10 Oda, S.J., Woods, B.G. and Foster, J. 1987. Microwave/Infrared drying of extruded ceramic forms; Journal of Canadian Ceramics Society, v.56, p.70-73.

11 Komameni, S. and Roy R. 1985. Titania gel spheres by a new sol-gel process; Materials Letters, v.3, no. 4, p. 165-167.

12 Haas, P.A. 1979. Heating of uranium oxides in a microwave oven; American Ceramics Society Bulletin, v.58, no. 9, p.873.

13 U.S. Patent 3,261,959. Filed 1962, issued July 1966. Apparatus for treatment of ore.

14a Nordin, L. and Salter, J.D. 1987. U.K. Patent Appl. GB 2188727. Sorting ore particles. DeBeers Industrial Diamond Division, London (Specific reference to Kimberlite ores.)* In a subsequent patent (GB2206213, Australia 8818195 Jan. 1989), obtainable on Derwent WPI Accession number 89-001793/01, the same writers claim a means for sorting particulate material according to the phase induced by microwave radiation transmitted through, or reflected from, a material. This is also a new microwave/mineral technique but at low (signal) power levels.

14b Kruesi, P.R. 1981. Process for the recovery of metals from their ores. European Patent Application 81302495:7; Publ. Number 0.041.841 (A1) Cato Research Corp., Wheatridge, CO.

15 Walkiewicz, J.W., Kazonich, G. and McGill, S.L. 1988. Microwave heating characteristics of selected Minerals and Compounds; Minerals and Metallurgical Processing, v.5, no.1., p. 39-42. (See also Journal of Microwave Power, v.23, no.1, p. 47-48).

16 McGill, S.L. and Walkiewicz, J.W. 1987. Applications of Microwave Energy in Extractive Metallurgy; Journal of Microwave Power, v.22, no.3, p. 175-177. (Summary).

17 McGill, S.L., Walkiewicz, J.W. and Smyers, G.A. 1988. The Effects of Power Level on the Microwave Heating of Selected Chemicals and Minerals; Symposium Proceedings of Materials Research Society, v.124, Paper M4.6 Now published in Reference [3].

18 Chen, T.T., Dutrizac, J.E., Haque, K.E., Wyslouzil, W. and Kashyap, S. 1984. The relative transparency of minerals to microwave radiation; Canadian Metallurgical Quarterly, v.23, no.3, p. 349-351.

19 Ulaby, F.T., Bengal, T., East, J., Dobson, M.C., Garvin, J. and Evans, D. March 1988. **Microwave dielectric spectrum of rocks**; University of Michigan, Ann Arbor; College of Engineering Report 023817-1-T.

20 Bodem, F. 1973. Ferromagnetization of FeS_2 (pyrite) contamination in natural kaolin resources by selective microwave heating; Proceedings of the European Microwave Conference, vol.2, paper C14.4, 4 pages (unnumbered), September 4-7; Brussels Univ. [Compendex 00410181].

21 As an example, the thermal conductivity of Al_2O_3 is (~) 35 W/m. K at 20°C, reducing to 7 at 500°C.

22 Ergun, S. *et al.* 1969. Separation method. U.S. Patent 3,463,310 [Enhanced magnetic properties for magnetic separation by electromagnetic heating].

23 Laurello, P.J. and Fritsch, C.A. 1974. Design and Economic Constraints of Thermal Rock Weakening Techniques; International Journal of Rock Mechanics, Mineral Science and Geomechanics, abstract 11, p. 31-39.

24 Arata, Y. *et al.* 1975. High power microwave plasma beam as a heat (Report IV) - Applications to cutting; Trans. Japan Welding Research Institute (JWRI), v.4, no.2, p.1-6. [Metadex 76: 530237].

25 Segsworth, R.F. and Lavers, J.D. 1979. Simple efficient plasma furnaces for melting and smelting; Proceedings for the 6th International Vacuum Metallurgy Conference (April), p.126-131. Rf induction plasmas have been investigated for nickel extraction from serpentine minerals. The analysis of P. Meubus [Canadian Journal of Chemical Engineering, 1973, S1, p. 440-446] is detailed.

26 Hoekstra, P. 1976. Rock, frozen soil and ice breakage by high frequency radiation: A review; Cold Regions Research Corps of Engineers and Eng. Lab. U.S. Army, Hanover NH: CRREL 76:36 (Oct. 1976). [GB2401:U58.M6.36].

27 Shibakova, V.S. *et al.* 1982. An outlook on the use of microwave energy for soil stabilizaton; New Delhi Proc. IV Congress Int. Ass. Eng. Geo. v.2, p. 267-273, and from references cited there.

28 Okamoto, R. 1982. Rock breaking by microwave radiation; New Delhi Proc. IV Congress Int. Ass. Eng. Geo. v.4, p.43-52.

29 Tejika, K. *et al.* 1987. Three dimensional analysis of a microwave heating furnace; Journal of Microwave Power, v.22, no.2, p.107-114. [Contains several references to nuclear waste—microwave studies. See also Krage, M.K. 1980. Apparatus and method for microwave heating in a kiln. U.S. Patent 4,189,629].

30 U.S. Patent 3,601,448. Method...fracturing concrete with microwave energy; 1971. Gas Dev. Corp., Chicago. [Information on microwave clinkering in a grooved resonant applicator (1983 study) is available from Dr. G. Roussy, Universite de Nancy 54037 Nancy Cedex, France].

31 Special issue: 1983. Energy Applications; J. Microwave Power, no.18, p.1-111.

32 Iskander, M.F. and DuBow, J.B. 1983. Time and frequency-domain techniques for measuring the dielectric properties of rocks: a review; *in* [31] v.18, p.55-74.

33 Vermeulen, F.E., Chute, F.S. and Cervenen, M.R. 1979. Physical modelling of the electromagnetic heating of oil sand and other earth-type and biological materials; Can. Elec. Eng. J., v.4, no. 4, p. 19-28.

34 Kalia, H.N. and Gresham, J.B. 1985. Commercialization of oil shales via in-situ retorting—some considerations; Am. Inst. Mining, Met., and Petroleum Engineers Trans., v.278, p.1141-1148.

35 Mallon, R.G. 1981. Economics of shale oil production by rf heating; Proc. 14th Oil Shale Symp. Colorado School of Mines, p.128-137.

36 Bluhm, D.D., Fanslow, G.E. and Nelson, S.O. 1986. Enhanced magnetic separation of pyrite from coal after microwave heating; IEEE Trans. MAG v.22, no.6, p.1887-1890.

37 Richardson, C.K., Markuszewski, R., Durham, K.S. and Bluhm, D.D. 1986. Effect of caustic and microwave treatment of clay minerals associated with coal; Am. Chem. Soc. Symp. Series 301 (Paper 38), p. 513-523.

38 Sutton, W.H. 1988. Microwave firing of high aluminum castables; Paper M6.6 in [3:287].

39 Roy, R., Komarneni, S. and Yang, L.J. 1985. Controlled microwave heating and melting of gels; J. Am. Ceram. Soc., v.68, no. 7, p.392-395.

40 Tobin, L.W. 1984. Microwave and ceramics: a process breakthrough; Advances in Ceramics, Am. Ceram. Soc. Proc. 1985 Ass. Meeting, p.156-169. (Compendex 01902222). [Excellent ceramic drying data. Original ideas were due to Von Hippel (MIT) 1954f].

41 Kamo, M. *et al.* 1983. Diamond synthesis from gas phase in microwave plasma; J. Cryst. Growth, v.62, no.3, p.642-644.

42 Kemer, E.L. and Johnson, D.L. 1985. Microwave plasma sintering of alumina; Am. Ceram. Soc. Bulletin, v.64, no.8, p.1132-1136.

43 Krage, M.K. 1981. Microwave sintering of ferrites; Ceramics Bulletin, v.60, no.11, p.1232-1234. [See also Okada, F. *et al.* (same title) 1986; Advances in Ceramics, in Am. Ceramic Soc., v.15, part 1, p.201-205].

44 Meek, T.T. and Blake, R.D. 1986. Ceramic-ceramic seals by microwave heating; J. Mat. Sci. Letters, no.5, p.270-274.

45 Ford, J.D. and Pei, D.C.T. 1967. High temperature chemical processing via microwave absorption; J. Microwave Power, v.2, no.2, p.61-64.

46 Wong, D. 1975. Microwave dielectric constants of metal oxides at high temperatures; MSc. Thesis, University of Alberta.

47 MacDowell, J.G. 1984. Microwave heating of nepheline glass-ceramics; Ceramics Bulletin, v.63, no.2, p.282-286.

48 Colomban, Ph. and Badot, J.C. 1978. Elaboration de ceramiques superconductrices anistropes ($Na^+\beta$ Al_2O_3) par chauffage microondes; Mat. Res. Bulletin, no.13, p.135-139.

49 U.S. Patent 4,147,911 (April 1979). Method for sintering refractories and apparatus—Nippon Steel, Japan.

50 Hassler, Y. and Johansen, L. 1988. Microwave heating of fused quartz to high temperatures in the fabrication process of optical fibres; *in* [3].

51 Meek, T.T., Blake, R.D. and Petrovic, J.J. 1987. Microwave sintering of Al_2O_3 and Al_2O_3-SiC whisker composites; Ceram. Eng. Sci. Proc., v.8, nos.7-8, p.861-871.

52 Ahmad, I., Chandler, G.T. and Clark, D.E. 1988. Processing of superconducting ceramics using microwave energy; *in* [3].

53 Johnston, D.A. 1970. Bibliography: microwave plasmas; J. Microwave Power, v.5, no.1, p. 17-22; v.5, no.1, p.192-197.

54 Westphal, W.B. and Sils, A. 1972. Dielectric Constant and Loss Data, Technical report AFML-TR-72-3339; reissue of TR64-250 Part 1 [MIT/NJIS fiche].

55 Fuller, B.D. and Ward, S.H. 1970. Linear system description of the electrical parameters of rocks; IEEE Trans. Geoscience Electronics (Jan.), p.7-18.

56 Tinga, W.R. 1988. Microwave dielectric constants of metal oxides, part 1; and part 2 (in press 1989); Electromagnetic Energy Reviews, v.1, no.5, p.2-6; v.2, no.1, p.1-6.

57 Westbrook, W.T. and Jefferson, R.H. 1986. Dissolution of samples by heating with a microwave oven in a teflon vessel for instrumental analysis; J. Microwave Power, v.21, no.1, p.25-32. [See also U.S. Patent, 1987; 4,683,867].

58 Walkiewicz, J.W., McGill, S.L. and Moyer, L.A. 1988. Improved grindability of iron ores using microwave energy; Paper M4.7 in [3].

59 Baillot, G. 1986. Road maintenance with a mobile microwave heating system; Paper 4.5, BNCE Proc. Heating and Processing Conference, Cambridge, UK. (Sept. 23-26).

60 Church, R.H. and Webb, W.E. 1986. A Measurement Technique for Determining the Dielectric Properties of Low Loss Materials Summary; J. Microwave Power, v.21, no.2, p.113-114.

61 Osepchuk, J. 1984. A History of Microwave Heating Applications; IEEE-MTT, v.32, no.9, p.1200-1224. [185 references, 30 illustrations].

62 Wei, C.K., Davis, H.T., Davis, E.A. and Gordon, J. 1985. Heat and mass transfer in water-laden sandstone: microwave heating; AIChE, v.31, no.5, p.842-848.

63 Yonscher, A.K. 1977. The universal dielectric response; Nature, no.267, p.673-679.

64 Bartnikas, R. and Eichhorn, R.M. eds. 1983., *in* Engineering Dielectrics Volume IIA: Electrical Properties of Solid Insulating Materials; Bartnikas, R. Dielectric Loss in Solids, p.3-117; and Tanaka, J. Composition and structure of dielectric solids, p.521-617; ASTM Publication 783, PCN 04-783000-21; 1916 Race St. Philadelphia, PA 19103.

65 Komarneni, S. and Roy, R. 1986. Anamolous microwave heating of zeolites; Materials Letter, v.4, no.2, p.107-110.

66 Manly, R. and Holmes, J. 1989. Minerals with a natural advantage; New Scientist, (March 25), p.39-43.

67 Roussy, G. 1986. Fluorite flotation under electromagnetic radiation; J. Microwave Power, no.22, p.241-242. *[A process to separate rare earths from other minerals

by slurrying with an electrolyte and induction heating (50-100 kHz) also suggests the use of microwave heating to enhance reduction. Potassium acetate is stated to be one possible eletrolyte. Details can be obtained on Derwent WPI Accession Number 83-09979K/05].

68 Roussy, G., Thiebaut, J.M., Charryne-Neel, M. 1985. A non-thermal model of microwave zeolite dehydration and paper drying; *in* IMPI Symposium Trans. (a summary of papers), p.220-222. [See also J. de Chie Physique, 1983., v.80, no.10, p.719-729; and R. Generale d'Electricite, Sept. 1983, no. 9, p.545-549.* See also a French patent (Jan. 1988) obtainable on Derwent WPI Accession Number 88-016137/03].

69 Beam, W.R. 1965. **Electronics of Solids;** McGraw-Hill, New York, p.28-43, p.386-388.

70 Glazun, B.A. and Zhilenkov, I.V. 1966. Dielectric properties of the system zeolite Zh-absorbed water; Russian J. Phys. Chem., v.40, no.6, p.734-735. [Referred to in [65]; probably the earliest analysis of Maxwell-Wagner relaxations in a zeolite].

71 Hu, C-I. J. 1979. Online measurements of the fast changing dielectric constant in oil shale due to high-power microwave heating; IEEE Trans. MTT, v.27, no.1, p.38-43.

72 Jain, R.C. September 1988. Microwave layer heating; PhD thesis, University of Alberta.

73 Bureau of Mines Technical Progress Report 120. April, 1983. [TN1 U584, No. 120, 1983].

74 Voss, W.A.G. and Jain, R.C. 1988. Unpublished data.

75 hp Product Note No. 8510-3.

76 Thorp, J.S., Evans, D. and Rad, N.E. 1987. High-temperature conductivity in MgO and Fe/MgO single crystals subject to 0.5 to 30 kHz; J. Materials Science, Letters, no.6, p.645-647.

77 Thorp, J.S., Bushell, T.G., Evans, D. and Rad, N.E. 1987. The temperature and frequency dependencies of permittivity and dielectric loss in reaction bonded silicon nitride; J. Materials Science, no.22, p.2641-2644.

78 Thorp, J.S. and Rad, N.E. 1981. The dielectric behavior of single-crystal MgO, Fe/MgO and Cr/MgO; J. Materials science, no.16, p.256-260.

79 Thorp, J.S. and Rad, N.E. 1986. The r.f. permittivity and dielectric loss of calcium, iron and magnesium silicides; J. Materials Science, Letters, no.5, p.157-158.

80 Thorp, J.S. and Rad, N.E. 1986. Microwave measurement of the temperature dependence of permittivity in molybdenum glasses, J. Materials Science, Letters, no.5, p.1321-1323.

81 Thorp, J.S., Rad, N.E. and Kulesza, B.I.J. 1985. RF permittivity and dielectric loss in binary molybdenum-phosphate glasses; J. Materials Science, Letters, no.4, p.895-897.

82 Parkhomenko, E.I. 1967. **Electrical Properties of Rocks**; Plenum Press, New York. A major source of low frequency (to rf) dielectric data.

83 From symposium meetings 1988. Not verified.

84 Glasses with transition metal oxides incorporated have a pronounced conduction mechanism due to electron "hopping". Electron mobility is then proportional to T^{-1} exp [-H/kT] where H, the activation energy, is (presumably) a temperature-dependent distribution function. Only a few cases have been measured. For a discussion, see [64:57] and references cited there.

85 Jain, R.C. and Voss, W.A.G. 1988. Dielectric data (2.9 GHz, 23-140°C) on $CaCl_2$ and NaCl susceptor pastes for microwave heating; Electromagnetic Energy Reviews, July, v.1, no.2, p.10-16.

86 Couderc, D., Giroux, M. and Bosisio, R.G. 1973. Dynamic high temperature complex permittivity measurements on samples heated via microwave absorption; J. Microwave Power, v.8, no.1, p.69-82.

87 Johnson, D.J. and Brodwin, M.W. 1988. Microwave sintering of ceramics; EPRI Project 2730-01, Interim Report March, 1987 (released ca. early 1988). See also same authors in [5]. Experimental data appears in above report.

88 Webb, W.E. and Church, R.H. 1986. Measurement of dielectric properties of minerals at microwave frequencies; U.S.D.O.I. Bureau of Mines RI #9035.

89 Bekhorskikh, S.M. 1986. Apparatus for measuring parameters of dielectric in microwave region at temperatures to 2300°K; *in* Instruments and Experimental Techniques, Trans Plenum Press, v.28, no.4, pt.2, p.888-891.

90 Petrov, E.I. et al. 1977. The possibilities of using UHF electromagnetic fields to improve ore concentrates; Electrochemistry in Industrial Processing and Biology, no.6, p.46-49. [UDC 622:778-868.8:622.344.6] (In English).

91 Recommendations for Testing Mineral Samples; Part II of Microwave Technology for Processing of Industrial Minerals, Their Products, Composites and Mixtures SSC File No. 0145AQ.23230-8-0110/S; AECL Chalk River Reference No. E0879, 1989.

92 Deer, W.A., Howie, R.A., Zussman, J. 1966. **An Introduction to the Rock-Forming Minerals**; Longman, London.